necessary for its occurrence.[11] The CO yield of unity places diisopropyl ketone in line with acetone[12] and diethyl ketone[13,14] both of which show $\Phi_{CO} = 1$ under conditions where the acyl radical is unstable. The anomalous behavior of di-*n*-propyl ketone, where only about half the absorbed quanta can be accounted for, seems therefore to be associated in some manner with the occurrence of the type II mechanism. Vibrational energy may be dissipated in a cyclic structure such as that suggested by Davis and Noyes[15] for methyl *n*-butyl ketone.

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[11] NOTE ADDED IN PROOF.—Further work supporting this hypothesis has been published recently, A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

The Stability of Metalloetioporphyrins toward Acids[1]

BY WINSLOW S. CAUGHEY[2] AND ALSOPH H. CORWIN

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In the Fe(III), Co(II), Ni(II) and Zn(II) complexes of etioporphyrin II the metal is displaced by concentrated sulfuric acid without decomposition of the porphyrin. The relative rates of metal displacement in sulfuric acid–acetic acid solution and in HCl–acetic acid solution are Co(II) > Ni(II) < Cu(II) << Zn(II). It is suggested that the stability order of these tetradentate "essentially covalent" compounds places the maximum stability in the Ni(II) complex. The kinetic data obtained for Cu(II) displacement were found to fit best the expression rate = k[copper etioporphyrin II]$^2(h_0)^4$.

The great stability of certain transition metal complexes of "fused-ring" compounds, such as the porphyrins and the phthalocyanines, has long been recognized. This stability is demonstrated by their extreme reluctance to undergo exchange and replacement reactions with radioactive metal ions in solutions[3-5] and by the necessity of using the strongest mineral acids for the displacement of certain metals.[6,7] Hill[8] reported that concentrated sulfuric acid was required for the displacement of Mn,Fe(III), Co(III), Ni(II) and Cu(II) from the respective hematoporphyrin complexes. The quantitative nature of the reaction was demonstrated when yields greater than 96% of etioporphyrin II (to be called Etio from now on) were obtained by treating copper etioporphyrin II (to be called CuEtio) with concentrated sulfuric acid.[9]

We have found that the Cu(II), Fe(III), Co(II), Ni(II) and Zn(II) complexes of Etio on treatment with concentrated sulfuric acid give immediately a sharp acid Etio spectrum and no other discernible bands. It was not feasible to obtain measurable rates by carrying out the reactions in an aqueous sulfuric acid medium due to the insolubility of these complexes in even slightly aqueous media. However, for the Ni(II), Cu(II) and Zn(II) complexes it was possible to follow the rates of metal displacement in sulfuric acid–acetic acid solutions. Acetic acid is an adequate solvent for the metallo Etio complexes and is sufficiently acidic to permit discrimination among very high acidities.[10,11] However, the Co(II) and Fe(III) complexes underwent considerable decomposition in this medium.

Qualitative experiments showed that in 0.5 *M* sulfuric acid in acetic acid at room temperature, Cu(II) and Zn(II) are removed very rapidly whereas Ni(II) is removed very slowly, if at all. In 1.0 *M* sulfuric acid in acetic acid Ni(II) removal was detected in ten minutes. In solutions less than 0.5 *M* in sulfuric acid Cu(II) is removed much more slowly than Zn(II). In HCl–acetic acid solutions Cu(II) and Co(II) were removed much faster than Ni(II). These qualitative experiments establish the relative rates of displacement in sulfuric acid–acetic acid solution and in HCl–acetic acid solution as Co(II) > Ni(II) < Cu(II) < < Zn(II).

In an attempt to replace Zn(II) with another metal ion, ZnEtio was refluxed for several hours in boiling pyridine with $NiAc_2$, with $CuAc_2$ and with $SnCl_2$. In no case was there a detectable replacement of Zn(II) with the metal ion in solution. Barnes and Dorough[5] found detectable replacement of Zn(II) by Cu(II) in one hour under these conditions with tetraphenylporphyrin complexes, whereas with the Etio complexes we could detect no replacement even after four days. We attribute this difference to the steric interference of the phenyl groups with the porphyrin ring.

The relative rates of the metal ion displacements *suggest* a stability order with Ni(II) the most stable—Co(II) < Ni(II) > Cu(II) >> Zn(II). Clearly, one is not justified in assuming a strict parallel between rates and equilibria. However, in this instance there is some additional support for this stability order for these square-planar "essentially covalent" complexes. Firstly, in certain iso-

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[1] Porphyrin Studies. XII; Paper XI, A. H. Corwin and V. L. Sydow, THIS JOURNAL, **75**, 4484 (1953). This paper was presented in part at the Chicago meeting of the American Chemical Society, September, 1953. It is from the doctoral dissertation of Winslow S. Caughey, The Johns Hopkins University.

[2] Standard Oil of Indiana Fellow, 1951–1952; Procter and Gamble Fellow, 1952–1953.

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[11] N. F. Hall and W. F. Spengeman, *ibid.*, **62**, 2487 (1940).

topic exchange experiments with Ni(II),[12] Cu(II)[13] and Zn(II)[14] complexes of salicylaldehyde–ethylenediimine and acetylacetone-ethylenediimine (both Ni(II) complexes were diamagnetic under the conditions of exchange) the rates of exchange were Zn(II) > Cu(II) > Ni(II). Secondly, the above stability order is suggested by shifts in the absorption maxima in the spectra of different metal complexes of the same chelating agent, *e.g.*, metallo Etios in pyridine: Ni(II) 550, 514 mμ; Cu(II) 560, 523 mμ; Zn(II) 572, 539 mμ; also, complexes of mesoporphyrin ester,[15] desoxyphylloerythrin ester,[16] phthalocyanine[17] and tetraphenylporphyrin.[18] A definite maximum shift to the blue in the case of the Ni(II) complexes is observed. Although a precise interpretation of the position of the band maxima *vs.* chelate stability is not feasible, in a series of like compounds of this sort it seems reasonable to assume that the amount of shift in absorption band(s) on chelation is related to the firmness of chelation. Evidence of such a relationship has been noted.[18,19]

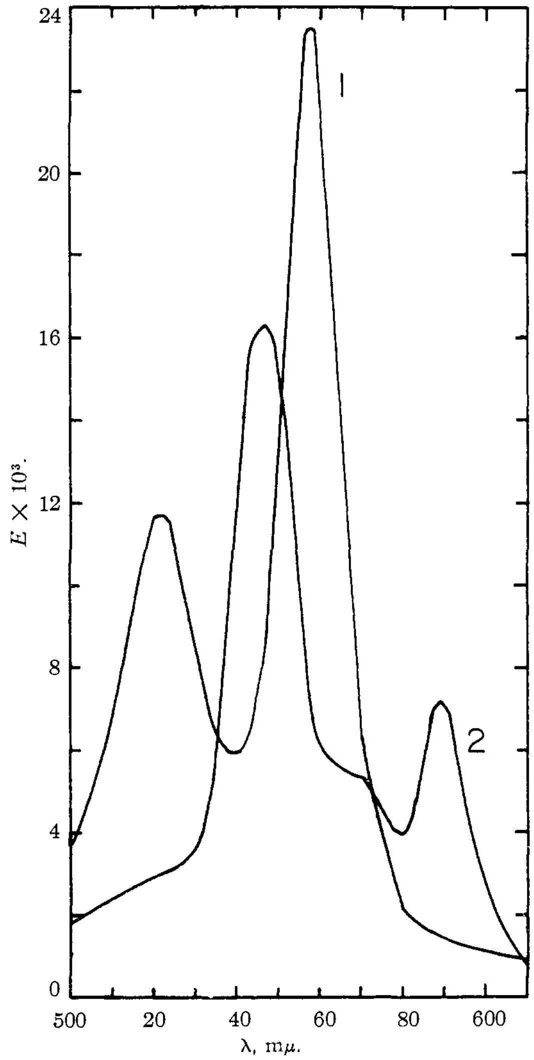

Fig. 1.—Visible absorption spectra in acetic acid solution containing 0.190 *M* pyridine, 0.200 *M* sulfuric acid and 3.06 $\times 10^{-6}$ *M* porphyrin: curve 1, CuEtio, curve 2, Etio; band width 1 mμ; temperature 30.0°.

Hence, it is reasonable to predict that further experimental work will show that these tetradentate "essentially covalent" square planar complexes follow a stability order which places maximum stability in the Ni(II) complex. This is in contrast to the order "irrespective of ligand" with Cu(II) the most stable—Co(II) < Ni(II) < Cu(II) >> Zn(II)—as noted by various investigators.[20–22] The presence of *two* stability orders could be ascribed to differences in bond type. Surely, in essentially all of the systems investigated in arriving at the order "irrespective of ligand" just mentioned, the Ni(II) complexes are "essentially ionic" (*i.e.*, paramagnetic) in the solvent media used regardless of their bond type as a solid.[12,23] Unfortunately bond type cannot be effectively followed in Cu(II) complexes. It would seem, however, that the Cu(II) complexes are less susceptible to solvent interaction which alters bond type than Ni(II) complexes. It would follow that in the highly stable covalent "fused-ring" compounds where solvent effect on bond type is small, Ni(II) complexes are more stable than Cu(II) complexes, but with the less stable complexes where solvent interaction (and solvent type) is important, Ni(II) complexes will be less stable than Cu(II) complexes.

Kinetics of Cu(II) Displacement.—In order to obtain more precise information about metal displacements by acid, we have studied the kinetics of Cu(II) displacement from CuEtio in AcOH solutions containing from 0.2 to 0.4 *M* sulfuric acid. Figure 1 shows that the spectra of CuEtio and the resulting acid salt of Etio are sufficiently different to permit following the reaction spectrophotometrically. However, since the extinction coefficients of CuEtio and acid Etio vary slightly with both porphyrin and sulfuric acid concentrations, it is difficult to follow the reaction directly by allowing the reaction to proceed in a spectrophotometer absorption cell. A satisfactory technique was devised whereby samples taken from the reaction mixture were quenched by neutralizing the sulfuric acid with pyridine. Beer's law deviations and medium effects were circumvented by adjusting the resulting quenched sample solutions for a given run to contain the same pyridine concentration, the same sulfuric acid concentration and the

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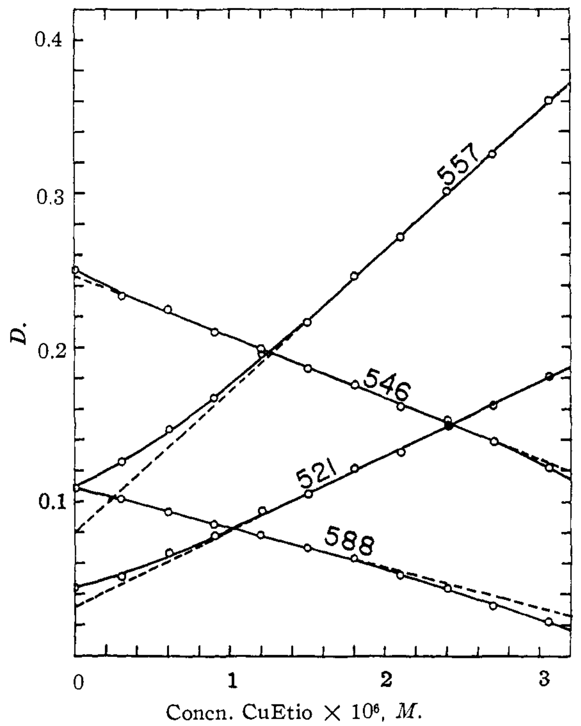

Fig. 2.—Standard optical density *vs.* [CuEtio] curves.

same total porphyrin concentration. Solutions of varying [CuEtio] and [Etio] with [$CuAc_2$] = [Etio] were prepared in the same medium and with the same total porphyrin concentrations as the resulting quenched sample solutions. In this manner standard optical density *vs.* [CuEtio] curves were established. Figure 2 shows such curves for the wave lengths 521, 546, 557 and 588 mμ.

The sulfuric acid concentration (0.01 *M*, *i.e.*, total pyridine concentration = 0.190 *M* and total sulfuric acid concentration = 0.200 *M*) in the resulting quenched sample solutions was rather critical since it was necessarily high enough to prevent the reverse reaction reforming some CuEtio from taking place, and low enough to effectively stop Cu(II) removal from the remaining CuEtio and to prevent interference from a competing side reaction. Though the displacement of Cu(II) from CuEtio is essentially quantitative at high sulfuric acid concentrations (above 0.20 *M*), at low sulfuric acid concentrations a very slow competing "Decomposition" reaction becomes important (Fig. 3). The rate of this side reaction increases as the concentrations of copper acetate and sulfuric acid increase. The rate dependence on the sulfuric acid concentration for this side reaction must be of a lower order than the Cu(II) displacement reaction since at concentrations of sulfuric acid above 0.2 *M* the rate of the side reaction is insignificant compared with the rate of Cu(II) displacement. As shown in Fig. 4 Etio is not affected by this side reaction. The nature of the reaction is left in doubt since the products are as yet unidentified.

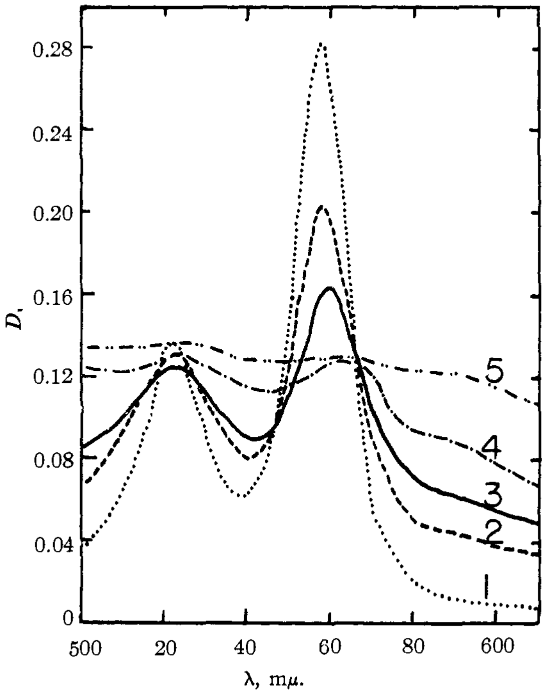

Fig. 3.—Changes in spectra during "decomposition" of CuEtio in AcOH soln. of low sulfuric acid concentration: CuEtio 2.2 × 10^{-6} *M*; H_2SO_4 0.038 *M*; copper acetate 2.25 × 10^{-6} *M*, temperature 30°; time (hours) after mixing: curve 1, 0.25; curve 2, 48; curve 3, 92; curve 4, 384; curve 5, 1176.

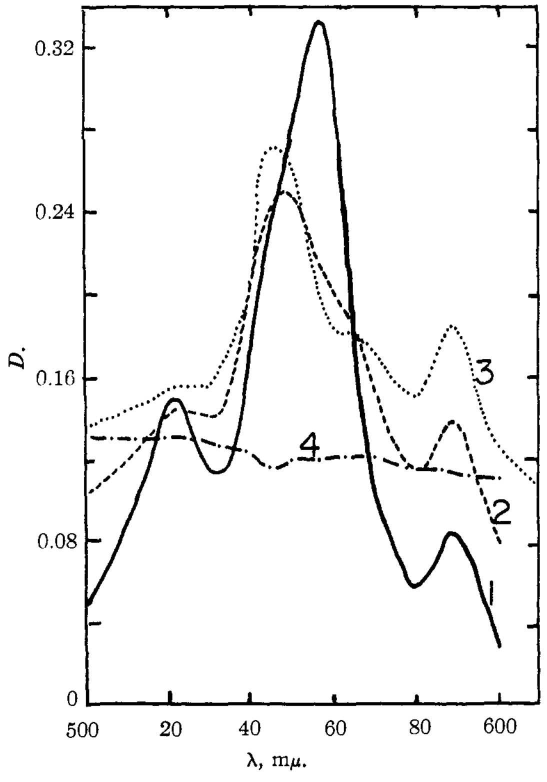

Fig. 4.—"Decomposition" of CuEtio in the presence of Etio: solvent acetic acid; CuEtio 2.2 × 10^{-6} *M*; Etio 2.0 × 10^{-6} *M*; sulfuric acid 0.038 *M*; copper acetate 4.5 × 10^{-6} *M*; temperature 30°; time (hours) after mixing: curve 1, 1.5; curve 2, 92; curve 3, 572. Curve 4 was obtained when the optical densities for 2.0 × 10^{-6} *M* Etio were subtracted from curve (3).

The optical densities of the quenched sample solutions at the wave lengths 521, 546 and 557 mμ were applied to the respective standard curves and the resulting values for [CuEtio] averaged. A plot of log [CuEtio] *vs.* time is not linear whereas the plot of 1/[CuEtio] *vs.* time is linear. The order of reaction was checked with the Powell plot[24] using dimensionless parameters and the plots of relative concentration (concentration at time *t*/initial concentration) *vs.* log *t* coincided exactly with the second-order curve in the Powell plot. It is therefore concluded that the reaction is second order in respect to CuEtio. Observed rate constants (k_{obsd}), as determined graphically (see Fig. 5), are listed in Table I. The values for acidity function (H_0) were obtained from a plot of the combined values of Paul and Hammett[10] and of Hall and Spengeman.[11]

TABLE I

RATES OF Cu(II) DISPLACEMENT

Temperature = 30.01 ± 0.01°

Run	$k_{\text{obsd}} \times 10^{-3}$, l. moles^{-1} min.$^{-1}$	H_2SO_4, *M*	H_0
1	0.715	0.216	−2.02
2	2.05	.267	−2.13
3	2.83	.287	−2.17
4	2.73	.287	−2.17
5	4.41	.312	−2.22
6	5.00	.328	−2.24

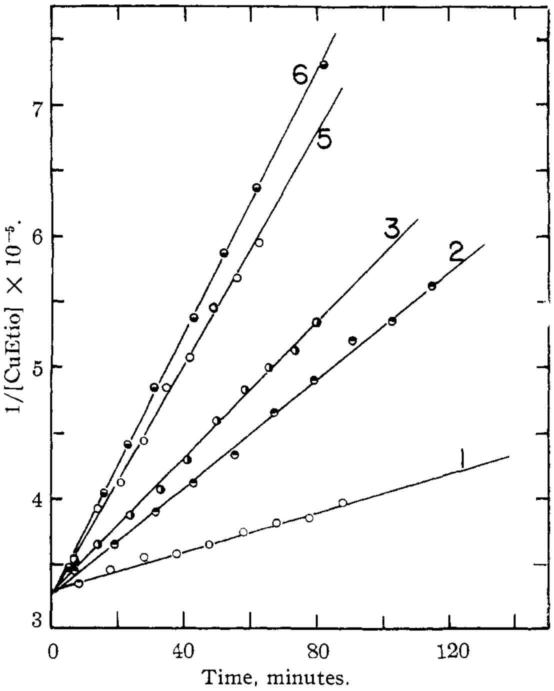

Fig. 5.—Cu(II) displacement reaction. Curve numbers represent runs of Table I.

The rate may therefore be satisfactorily expressed as

$$-\frac{d\,[\text{CuEtio}]}{dt} = k_{\text{obsd}}\,[\text{CuEtio}]^2 \qquad (1)$$

Table I shows that each individual run is pseudo second order. The observed rate constants increase with the sulfuric acid concentration and can be related to the actual rate constant (*k*) by expression 2

$$k_{\text{obsd}} = k \times f_{\text{acidity of soln.}} \qquad (2)$$

Although the significance of attempting to accurately determine such a high order dependence on acidity may be open to question, it is interesting to note that a plot of log k_{obsd} *vs.* H_0 results in a very close fit for a straight line with a slope of 4 (note Fig. 6 where the broken lines represent slopes of 3 and 5). Similarly, a plot of log k_{obsd} *vs.* log [sulfuric acid] gives a good fit for a straight line with a slope of 5. Thus expression (2) becomes

$$k_{\text{obsd}} = k(h_0)^4 \qquad (3)$$

where $H_0 = -\log h_0$ and $h_0 = a_{H^+}f_B/f_{BH^+}$. The rate of the over-all reaction can be expressed as

$$-\frac{d[\text{CuEtio}]}{dt} = k[\text{CuEtio}]^2\,(h_0)^4 \qquad (4)$$

The strict applicability of h_0 in this case is somewhat questionable.[25] As originally defined by Hammett,[26] the acidity function expressed the

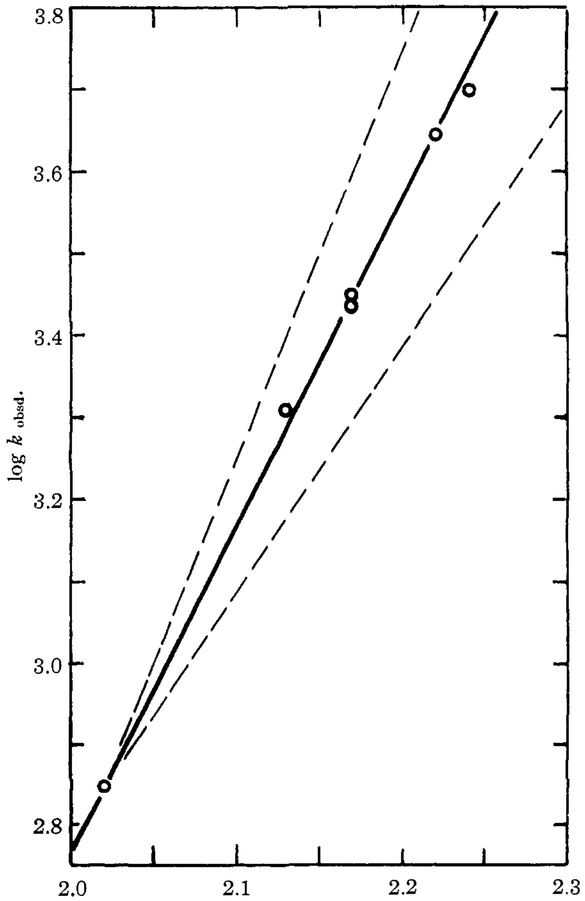

Fig. 6.—Rate dependence of Cu(II) displacement on acidity function. Solid line has slope = 4; broken lines have slopes of 3 and 5.

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tendency for a solution to transfer a proton to a *neutral* base. In this case the first proton would add to a neutral base but not the subsequent protons. It is suggested that the points of proton addition in the formation of a transition state involving two CuEtio molecules are likely to be sufficiently isolated to permit the use of H_0 in this fashion. Other examples considered to have a high order dependence on h_0 are the decompositions of oxalic and citric acids showing an order of 2 and of triphenylacetic acid with an order of 3.

Therefore, although the data for this type of reaction are as yet of limited scope, they do indicate a high dependence of the rate on the acidity of the solution, as might well be expected from the nature of the reaction where four protons are replacing the Cu(II). However the second-order dependence on the [CuEtio] is not a result one would necessarily expect. A suggested manner in which two molecules of CuEtio and four protons are involved in the rate determining formation of the transition state is a rapid reversible equilibrium involving CuEtio and diprotonated CuEtio followed by the interaction of two diprotonated CuEtio molecules to form the transition state and thence on to the products, as shown in equations (5) and (6).

$$\text{CuEtio} + 2\text{H}^+ \rightleftarrows \text{CuEtio}\cdot 2\text{H}^+ \qquad (5)$$

$$2\text{CuEtio}\cdot 2\text{H}^+ \longrightarrow \text{Products} \qquad (6)$$

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Experimental

Relative Rates of Metal Ion Displacement from Metalloetioporphyrins.—Approximately 0.1 mg. of the respective MEtio was dissolved in 1 ml. of the solvent in question and the spectral changes were observed with a hand spectroscope.

Kinetics of Cu(II) Displacement from CuEtio.—The reaction flask, a 250-ml. 3-necked round bottom flask equipped with a stirrer, a drying tube ("Drierite") and a glass stopper, was submerged up to the necks in a water-bath maintained at 30.01 ± 0.01°. To this flask 100 ml. of a 9.46×10^{-6} *M* solution of CuEtio in acetic acid was added and at zero time 50 ml. of a sulfuric acid–acetic acid solution was added with rapid stirring. Both of these solutions were at the water-bath temperature. At intervals of about nine minutes the stopper was removed, a sample of approximately 12 ml. was drawn into a sampler and the sampler tube was inserted in the neck of a 25-ml. volumetric flask containing the quenching solution. This quenching solution contained the amounts of pyridine and sulfuric acid which would give a quenched sample solution of precisely the same total porphyrin, pyridine and sulfuric acid concentrations as the solutions used for the standard optical density *vs.* [CuEtio] curves. At a recorded time the sample was forced into the quenching solution. Emptying the sampler required about 30 seconds and the mid-point was considered to be the time of quenching. After being thoroughly shaken the quenched sample solution was diluted to volume with AcOH and placed in an air-bath at 30.0° until the spectrum was taken. After all the samples for a run had been collected, the optical densities at thirteen wave lengths were measured by a Beckman DU spectrophotometer at 30.0°, using matched 5-cm. fused-silica cylindrical cells. A band width of 1 mμ was used throughout. The cell compartment was a standard assembly of the Beckman instrument modified to keep the compartment at constant temperature. The modification consisted of a water jacket for circulating water of constant temperature, insulation, a small stirrer for air circulation within the compartment and a thermometer. In this fashion the temperature was maintained at 30.0 ± 0.15°.

Materials. Etioporphyrin II.—1.292 grams of synthetic Etio was dissolved in $CHCl_3$ and chromatographed three times through an alumina column using $CHCl_3$ as the eluant. In each case the Etio fraction was concentrated at a temperature below 30° under vacuum while "prepurified" nitrogen was bled into the solution. After precipitating from the final concentrate plus methanol, the Etio was dried at 110° and 35 mm. of Hg (yield = 0.895 g.). *Anal.* Calcd.: C, 80.29; H, 8.00; N, 11.7. Found: C, 80.29, 80.21; H, 7.85, 8.13; N, 11.7. The visible spectrum in dioxane compares favorably with previously reported values[27,28]—extinction coefficients $\times 10^{-3}$: 498 mμ (14.2), 530 mμ (10.3), 567 mμ (6.75), 622 mμ (5.80).

Copper Etioporphyrin II.—The crude CuEtio, prepared from Etio and copper acetate in hot glacial acetic acid after Erdman and Corwin, was chromatographed on an alumina column using $CHCl_3$ as the eluent. The CuEtio fraction was concentrated under vacuum below 30° while "prepurified" nitrogen was bled into the solution. After addition of methanol the concentrate produced bright red needles on standing in the cold. This product was twice recrystallized in the manner described by Erdman and Corwin. The spectra and analyses indicate a high state of purity. *Anal.* Calcd.: C, 71.14; H, 6.72. Found: C, 70.99, 70.99; H, 7.07, 6.75.

Metalloetioporphyrins (Fe(III), Co(II), Ni(II), Zn(II)).—These MEtios are considered apart from CuEtio because they were not as well purified as the CuEtio. The general procedure followed was essentially that used by Hill[8] with a few modifications. The procedure used in the case of ZnEtio will be described in detail as an example. After 65 ml. of acetic acid had been refluxed under "prepurified" nitrogen for 20 minutes in a 100-ml. flask, 40 mg. of Etio was washed into the flask with 10 ml. of deaerated acetic acid and the resulting solution refluxed for ten minutes. After the rapid addition of 60 mg. of $ZnAc_2\cdot 2H_2O$ the solution was refluxed for one-half hour. The reaction mixture was cooled very slowly. The resulting brilliant red crystals were collected on a needle filter and washed thoroughly with 50% water–acetic acid. A hot solution of the crude precipitate in 10 ml. of $CHCl_3$ was filtered leaving a few mg. of undissolved material on the filter. To the center of the hot filtrate in a 30-ml. erlenmeyer flask was added 10 ml. of hot deaerated acetic acid. The flask was placed in a beaker of hot water and allowed to cool slowly. The needles formed were collected, washed with 50% water–acetic acid and dried at 100° *in vacuo*. *Anal.* Calcd.: C, 70.90; H, 6.70. Found: C, 70.74; H, 6.82. The procedure for the preparation of ZnEtio is satisfactory for NiEtio as well, but for the other MEtios noted above strict precautions to prevent air oxidation were taken if the divalent complex was to be prepared.

Acetic Acid.—The reagent grade acetic acids used were found unreliable in regard to water content and metallic impurities. Therefore, reagent grade acetic acid was refluxed for several hours while "prepurified" nitrogen was bled into the still pot and then distilled through a 3 ft. glass bead column. The first and last quarters of distillate were discarded. The purified product was stored under nitrogen. All batches contained less than 0.15% water as determined by Karl Fischer titration. The acetic acid used in the rate studies contained 0.063% water.

Pyridine.—1500 ml. of pyridine (C.P. J. T. Baker analyzed containing about 0.7% water) and 585 ml. of benzene (Mallinckrodt A. R.) were distilled through a 14-inch helices-packed column. The distillate coming over below 112° was discarded and about 1200 ml. of dry pyridine (0.014% water) collected.

Sulfuric Acid.—100% sulfuric acid was prepared according to the "Fair and Foggy" method of Kunzler.[29]

Dioxane.—Technical dioxane was refluxed over sodium and distilled just before use.

Chloroform.—Chloroform of reagent grade was refluxed over calcium oxide and distilled just before use.

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