Table VI. Summary of Derived Parameters for the Hydrolysis of Dihalides

Halide	$k \times 10^5$, sec^{-1} (25°)	ΔH^*_{25}, cal/mole	ΔS^*_{25}, cal/mole deg	ΔC_p,* cal/mole deg	Ref
2,2-Dibromopropane	4.618	26,940	12.0	−81	*a*
2,2-Dichloropropane	0.9088	27,000	8.9	−75	*a*
		25,120 (50°)	2.9 (50°)		*a*
2-Bromo-2-chloropropane	17.81	25,950	11.3	−94	*a*
t-Butyl chloride	2975	22,550	10.1	−83	3
2-Bromopropane	0.3816	25,830 (25°)	4	−59	*b*
2-Chloropropane	0.02114	24,940 (50°)	−5.3	−38	*b*

[a] This work. [b] R. L. Heppolette and R. E. Robertson, *Can. J. Chem.*, **44**, 677 (1966).

the changes in ΔC_p^* on the addition of ethanol to water compared to the similar effect where the equilibria of weak acids is concerned.[22] We know that the ΔH^* decreases at about 80–100 cal/deg. This may be achieved with increasing temperature through (1) a destabilization of the initial state solvation shell or (2) through an increase in the solvation energy of the cation formed at the transition state, as a consequence of a decrease in water–water interaction. Our working hypothesis (1) excludes 2, but does not exclude some contribution to ΔC_p^* from the solvation of the anion. We do not believe the latter contribution to be large.

Experimental Detail

2,2-Dibromopropane was synthesized by a modification of the method of Kharasch, Zimmt, and Nudenberg,[23] bp 116–118°, $n^{24.5}$D 1.4959. *Anal.* Calcd: C, 17.82; H, 2.97; Br, 79.21. Found: C, 17.98; H, 2.97; Br, 79.12. A sample hydrolyzed in water for 25 min at 60° gave 49.47% of the theoretical amount of bromide, *i.e.*, one bromide is removed. Solvolysis of a larger sample and separation of the product by extraction with CCl_4 showed that 2-bromopropene (vpc and nmr) was the only product in other than trace amounts. When allowed to react with water at 130° under pressure for 36 hr the latter gave acetone as characterized by the DNPH derivative.

2,2-Dichloropropane was synthesized by dropping acetone on PCl_5 by the method of Leitch and Morse[24] and pumping off the *gem*-dihalide at room temperature through a Stock trap. The product was redistilled, bp 68–69°, washed with water, dried, and shown to have a single peak on vpc.

2-Bromo-2-chloropropane was synthesized by a modified Kharasch method and purified by distillation, bp 92°, n^{23}D 1.4539. Hydrolysis gave 1 equiv of Br^- per mole of the dihalide, and essentially a single vinyl product, 2-chloropropane. Since the latter was very unreactive in the experimental range, the presence of small amounts of this product in the *gem*-dihalide (nmr and vpc) did not influence the rates.

Rate data were determined by a conductance method[25] utilizing the relation

$$\log (1/R_2 - 1/R_1) = kt - C$$

Since our interest is in the temperature dependence of the rate, the effect of this approximation on the derived parameters was assumed to be unimportant. In any case, the differences in the rates between values so determined and checked against calibrations were not judged to be significant.

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(22) D. H. Everett and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **35** 1380 (1939).

(23) M. S. Kharasch, W. S. Zimmt, and W. Nudenberg, *J. Org. Chem.*, **20**, 1430 (1955).

(24) L. Leitch and A. Morse, *ibid.*, **23**, 991 (1958).

(25) R. L. Heppolette and R. E. Robertson, *J. Am. Chem. Soc.*, **83**, 1834 (1961).

Electrochemical Studies of Some Iron–Protoporphyrin Complexes

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Abstract: The electrochemistry of several complexes of iron-protoporphyrin has been studied by chronopotentiometry, microelectrode voltammetry, and controlled-potential coulometry using platinum electrodes, and by polarography and cyclic voltammetry using mercury electrodes. Complexing agents investigated include cyanide ion, pyridine, picoline (β and γ), water, and hydroxide ion. The electroreduction of these monomeric complexes, corresponding to the reduction of iron(III) to iron(II), proceeds as a reversible, one-electron change. From the data obtained, it is possible to establish the form of the various complexes and the equilibrium constants for the formation of several complexes. Adsorption on the electrode surface of some of the complexes has been measured by both chronopotentiometry and cyclic voltammetry.

In alkaline ethanolic aqueous solution and in the presence of suitable complexing agents, iron-protoporphyrin forms complexes of essentially octahedral symmetry. Four coordination sites of the iron are occupied by the pyrrole nitrogens on the protoporphyrin ring; the ring thus defines the *X–Y* plane of the complex. This feature is drawn schematically in Figure 1. The two remaining coordination positions

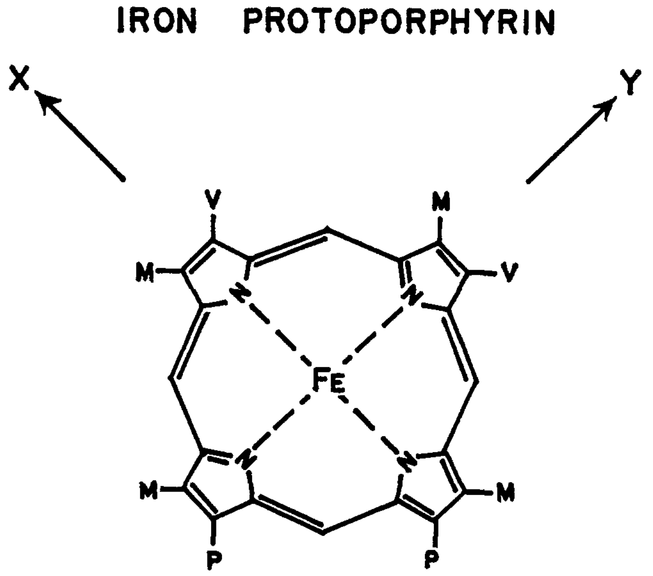

Figure 1. X–Y plane of iron–protoporphyrin: M = methyl, V = vinyl, P = propionic acid. The Z axis is perpendicular to the plane of the paper.

on the Z axis are available for further complexing. This work is concerned with the effects on electrochemical parameters caused by variations in the ligands occupying the Z positions.

In alkaline solutions, the complexes under investigation exist as anionic species due to the ionization of the propionic acid side chains of protoporphyrin. If two pyridine molecules occupy the Z-axis sites of the iron(III) complex, the species is named the *trans*-dipyridylprotoporphyrinferrate(III) ion. However, the more common literature nomenclature[1–3] will be followed here. Thus, the above complex can be simply called pyridine hemichrome. The *trans*-dipyridylprotoporphyrinferrate(II) ion can be called pyridine hemochrome. The terms hemichrome and hemochrome, which refer to the complexes of iron(III) and iron(II), respectively, are reserved for those complexes characterized by the red color ordinarily found when the ligands involved contain nitrogen and are capable of π interaction with the central metal ion. If two different ligands occupy the Z position, both will be named (*i.e.*, cyanopyridine hemichrome).

Studies of the electron-transfer reactions of metalloporphyrins are of considerable interest since reactions of this type are important steps in the transfer of energy by respiratory enzymes. The cytochrome system found in mitocondria is the classic example. The participation of Z-position ligands in these unusually rapid electron-transfer mechanisms has been proposed.[4]

The solution chemistry of iron–porphyrin complexes of several ligands has been studied[1] by means of zero-current (classical) potentiometry and spectrophotometry. Work of this type has been collected and summarized by Clark[2] and by Falk.[3] Although potentiometric data are relatively simple to collect, misinterpretations are not unlikely since certain species may exist in solution but not be detectable unless a complete polarogram is recorded, as is illustrated, for instance, in Figure 6. The possibility of unnoticed errors due to electrode surface phenomena is also of importance. Overlapping spectra cause difficulties with spectrophotometric measurements.

Recently, Jordan and Bednarski reported a dropping mercury electrode polarographic study of iron–protoporphyrin in dilute aqueous potassium hydroxide.[5] These workers concluded that under their solution conditions a ferric protoporphyrin chelate dimer undergoes a reversible two-electron reduction yielding two molecules of the monomeric *trans*-diaquoprotoporphyrinferrate(II) ion.

Experimental Section

Solutions of the iron(III)–protoporphyrin complexes were generally prepared by dissolving the desired quantity of chlorohemin (Nutritional Biochemical Corp.) in a 30% ethanolic aqueous solution of the complexing agent. All chemicals used, other than chlorohemin, were reagent grade. Test solutions were 1 M in sodium nitrate, which acted as supporting electrolyte. Borax (0.03 M) or phosphate (0.05 M) buffers were used to adjust the pH when necessary. Ethanol was added to the solutions to assure solubility of the more insoluble of the complexes, for instance, pyridine hemochrome. It had the added effect of inhibiting the formation of dimers which exist[5] under similar solution conditions, but without alcohol. The concentration of complexing agent required to form the desired complex varies, of course, with the stability of the complex. For a solution 1 mM in the iron–porphyrin, 0.5 M sodium cyanide, 2.0 M pyridine, or 2.0 M picoline is sufficient to form the respective diligand complexes.

The chronopotentiometric apparatus was conventional and has been described elsewhere.[6] The working electrode was a horizontal, unshielded platinum disk with a projected area of 0.224 cm^2. For the measurement of short transition times, a Tektronix 535A oscilloscope was used instead of the strip chart recorder.

Polarograms were recorded using a Sargent Model XV polarograph equipped with either a rotating platinum electrode assembly (600 rpm) or a conventional dropping mercury electrode (dme). Controlled potential coulometry experiments were carried out using an Analytical Instruments potentiostat and current integrator. The design of the electrode and cell have been previously reported.[7]

The potential control unit for the cyclic voltammetry experiments consisted of a Wenking Model 61R fast rise potentiostat fed by a triangle wave generator which has been described.[8] The cell for these hanging mercury drop experiments was a Metrohm Herisau microfeeding apparatus E-410 equipped with an isolated stout platinum wire which served as the auxiliary electrode. Cyclic voltammograms were recorded with a Hewlett-Packard Model 130B oscilloscope and Model 196A oscilloscope camera. All measurements requiring constant temperature were made at 25.0 ± 0.1°, and all solutions were deaerated with a stream of prepurified nitrogen which was passed through a portion test solution before entering the cell. This procedure prevents the solution in the cell from losing volatile components such as alcohol or HCN during deaeration. Potentials are reported with reference to the saturated calomel electrode, which was used in all experiments except the cyclic voltammetry. A silver–silver chloride reference electrode was used in this case. In the polarographic and cyclic voltammetric experiments, an agar salt bridge was used to contact the reference electrode to the test solution. For chronopotentiometry a fiber type sce was employed.

In order to obtain consistent results with platinum electrodes, it was necessary to pretreat the electrode in such a way that a clean but "activated" electrode surface was obtained.[9] This was generally accomplished by oxidizing the electrode at +1.5 v *vs.* sce for 15 min and then removing the surface oxygen or oxide coating

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(1) J. Shack and W. M. Clark, *J. Biol. Chem.*, **171**, 143 (1947).

(2) W. M. Clark, "Oxidation Reduction Potentials of Organic Systems," Williams and Wilkins, Baltimore, Md., 1960, Chapter 8.

(3) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier Publishing Co., New York, N. Y., 1964.

(4) D. W. Urry and H. Eyring, *Proc. Natl. Acad. Sci. U. S.*, **49**, 253 (1963).

(5) J. Jordan and T. M. Bednarski, *J. Am. Chem. Soc.*, **86**, 5690 (1964), and private communication.

(6) D. G. Davis and J. Ganchoff, *J. Electroanal. Chem.*, **1**, 248 (1960).

(7) D. G. Davis, *ibid.*, **1**, 73 (1959).

(8) D. J. Orgeron, Thesis, Louisiana State University in New Orleans, 1965.

(9) F. C. Anson, *Anal. Chem.*, **33**, 934 (1961).

Table I. Electrochemical Data for Various Hemichromes

Complex[a]	Polarography $E_{1/2}$,[b] v	Polarography Slope[c]	Controlled-potential coulometry n	Chronopotentiometry $E_{\tau/4}$,[b] v	Chronopotentiometry Slope[c]
$H(CN)_2$	−0.499	0.061	1.01	−0.495	0.060
$H(CN)_2$, no ethanol	−0.413	0.059	1.01	−0.420	0.060
$H(py)_2$ (pH 7.9)	−0.128	0.060	0.98	−0.129	0.059
H(CN)(py)	−0.360	0.061	1.01	−0.358	0.061
H(pic, β or γ) (pH 8)	−0.147	0.059	0.99	−0.145	0.060

[a] H signifies iron(III)-protoporphyrin; py, pyridine; pic, picoline. [b] Potentials *vs.* sce refer to complexes in 30% ethanolic solution except where noted. [c] A plot of log $[(i_d - i)/i]$ for polarography or log $[(\tau^{1/2} - t^{1/2})/t^{1/2}]$ for chronopotentiometry *vs.* potential was used to test "Nernstian" reversibility. A slope of 0.059 indicates a reversible one-electron reduction, in view of evidence obtained by controlled potential electrolysis supporting the one-electron change.

at a reducing potential such as −0.4 v *vs.* sce just before the chronopotentiogram or polarogram was recorded. Pretreatment was done in a separate electrolyte solution in the early stages of the work. However, it was found that the electrode could be pretreated in the test solution with no apparent undesirable effects.

Results and Discussion

Table I summarizes the data obtained with platinum electrodes for a variety of complexes. The dicyano, cyanopyridyl, and dipyridyl complexes were studied extensively in this part of the work.

Cyanide Hemichrome. The reduction of the cyanide hemichrome proceeds as a reversible, one-electron change as indicated in Table I. Moreover, reverse current chronopotentiometric data (in the 10- to 50-sec range) showed that the reverse transition time was equal to one-third of the forward electrolysis time, and the value of the reverse $E_{\tau/0.215}$ was essentially equal to the forward $E_{\tau/4}$ as expected by theory.[10] Controlled-potential coulometry not only indicated the electron change to be one, but the spectra of the cyanide hemochrome thus produced was the same as that previously reported.[3] The technique of controlled potential electrolysis was found to be an excellent and easy method for the production of hemochromes without the necessity of adding extraneous chemical agents.

In order to assure that no kinetic complications were involved in the electrode reaction mechanism, a study was made of the effect of variation of current density and hemin concentration on the chronopotentiometric constant, $i_0\tau^{1/2}/C$, where i_0 is the current density in amperes per square centimeter, τ is the transition time in seconds, and C is the concentration in moles per cubic centimeter. The aqueous ethanol (30% by volume) electrolyte solution for this study was 1 *M* in sodium nitrate and 0.5 *M* in sodium cyanide. The pH of this solution was 10.5. No effects that could be attributed to kinetic phenomena were observed, but useful information was obtained. At large values of τ (2 to 50 sec), $i_0\tau^{1/2}/C$ was essentially constant indicating simple diffusion control of the electrode reaction. (Actually slight variations in $i_0\tau^{1/2}/C$ at τ's near 50 sec were noticed; these are caused by convection and nonlinear diffusion.[11]) At short transition times, $i_0\tau^{1/2}$ increases with decreasing τ (increasing i_0) as is shown in Table II. Possible causes of this phenomena include double-layer charging, reduction of surface oxygen at the electrode–solution interface, and the reaction of electroactive-adsorbed species on the electrode surface.[12] For the case under consideration here, little effect of surface oxygen is expected due to the potential range being investigated and the electrode pretreatment procedure. Double-layer charging can be shown to make only a minor contribution to the effect observed. Thus, adsorption may be considered as the main contributor to the increase in $i_0\tau^{1/2}$ with decreasing τ.

Table II. Chronopotentiometry of Cyanide Hemichrome[a]

Concn, mole/cm³	τ, sec	$i_0\tau^{1/2}/C$, amp sec$^{1/2}$ cm³/mole
4.82×10^{-6}	3.30	113
	0.350	119
	0.175	124
	0.086	137
	0.024	166
	0.0125	195
1.21×10^{-6}	1.85	140
	0.38	152
	0.13	175
	0.040	234
3.00×10^{-7}	0.92	222
	0.42	247
	0.18	283

[a] 1.0 *M* $NaNO_3$, 0.5 *M* NaCN, 30% alcohol; electrode area = 0.224 cm².

Several theoretical models for chronopotentiometry involving adsorption of electroactive species have been proposed.[13] There are three models which assume no particular adsorption isotherm, but which require only that adsorption equilibrium be established before electrolysis. One[13] assumes that the adsorbed layer is completely electrolyzed *before* electrolysis of the diffusing species begins. The next[14,15] assumes that the adsorbed layer is electrolyzed *after* electrolysis of the diffusing species is completed. The last[13] assumes that a simultaneous reaction of adsorbed and diffusing species takes place in such a way that a constant fraction of the applied current is consumed by each species. The mathematical treatment of data for the evaluation of the quantity of adsorbed species (Γ) and the diffusion coefficient of the diffusing species (*D*), based on each of the above models, has recently been reviewed by Tatwawadi and Bard.[16] Our data collected from the chrono-

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(10) W. H. Reinmuth, *Anal. Chem.*, **32**, 1514 (1960).
(11) A. J. Bard, *ibid.*, **33**, 11 (1961).
(12) A. J. Bard, *ibid.*, **35**, 340 (1963).
(13) W. Lorenz, *Z. Elektrochem.*, **59**, 730 (1955).
(14) F. C. Anson, *Anal. Chem.*, **33**, 1123 (1961).
(15) W. H. Reinmuth, *ibid.*, **33**, 322 (1961).
(16) S. V. Tatwawadi and A. J. Bard, *ibid.*, **36**, 3 (1964).

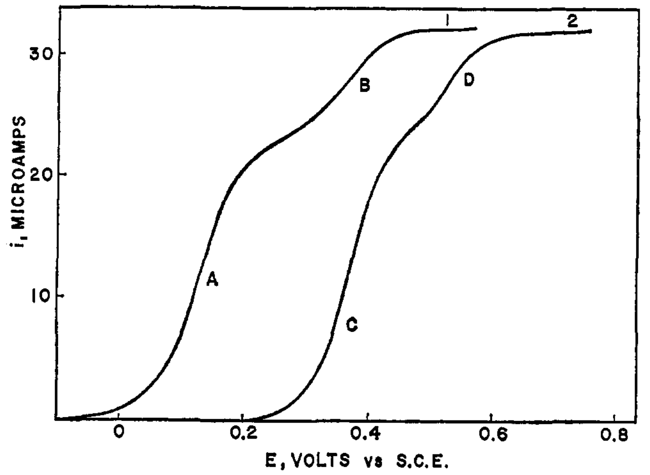


Figure 2. Polarograms of hemichromes with a rotating platinum electrode. Polarogram no. 1: 0.81 × 10^{-3} M hemin, 2.0 M pyridine, 3 × 10^{-4} M NaCN, 1 M $NaNO_3$, 30% ethanol. Polarogram no. 2: 0.81 × 10^{-3} M hemin, 2.0 M pyridine, 1 × 10^{-2} M NaCN, 1 M $NaNO_3$, 30% ethanol. A, reduction of pyridine hemichrome; B, reduction of cyanopyridine hemichrome; C, reduction of cyanopyridine hemichrome; D, reduction of cyanide hemichrome.

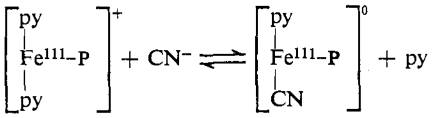
potentiometric analysis of cyanide hemichrome lead to the results shown in Table III. The variation of Γ and D with concentration are similar to those found previously for other substances.[17] It may be, however, that the rather large variation of D is partially due to weak aggregate formation as illustrated by previous diffusion studies.[1]

Table III. Amount of Cyanide Hemichrome Adsorbed (Γ) and Diffusion Coefficient (D) Calculated by Different Theoretical Models[a]

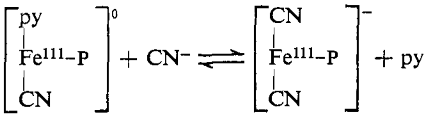
	Electrolyzed absorbed layer				Simultaneous electrolysis	
	First		Last			
C^b	Γ^c	D^d	Γ^c	D^d	Γ^c	D^d
4.82	8	1.5	3	1.5	5	1.5
1.21	4	2.1	2	2.1	3	1.8
0.30	2	4.3	1	4.1	2	3.6

[a] 1.0 M $NaNO_3$, 0.5 M NaCN, 30% alcohol; electrode area = 0.224 cm². [b] $C \times 10^6$ moles/cm³. [c] $\Gamma \times 10^{10}$ moles/cm². [d] $D \times 10^6$ cm²/sec.

Cyanopyridine Hemichrome. As indicated in Table I, both the pyridine hemichrome and the cyanopyridine hemichrome undergo reversible, one-electron reductions. Polarography with a rotating platinum electrode was found to be a particularly useful device for study of the reactions



$$\left[\begin{array}{l}\text{py}\\ |\\ \text{Fe}^{\text{III}}\text{–P}\\ |\\ \text{py}\end{array}\right]^{+} + \text{CN}^- \rightleftharpoons \left[\begin{array}{l}\text{py}\\ |\\ \text{Fe}^{\text{III}}\text{–P}\\ |\\ \text{CN}\end{array}\right]^{0} + \text{py} \qquad (1)$$

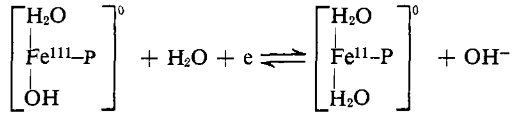


$$\left[\begin{array}{l}\text{py}\\ |\\ \text{Fe}^{\text{III}}\text{–P}\\ |\\ \text{CN}\end{array}\right]^{0} + \text{CN}^- \rightleftharpoons \left[\begin{array}{l}\text{CN}\\ |\\ \text{Fe}^{\text{III}}\text{–P}\\ |\\ \text{CN}\end{array}\right]^{-} + \text{py} \qquad (2)$$

Here py symbolizes pyridine, P denotes the protoporphyrin ring, and the charges are calculated neglecting the contribution of the propionic acid groups attached to the porphyrin ring. Such polarograms are illustrated in Figure 2. It may be seen that the complex with one cyanide ion and one molecule of pyridine may be easily identified. This complex has been previously studied[1,18] under slightly different conditions. In this work, higher concentrations of iron–protoporphyrin were used in order to minimize the relative effect of undesirable polarographic reactions due to small amounts of oxygen or other contributors to the residual current. These higher concentrations dictated the use of ethanol (30%) to render soluble the pyridine hemochrome which otherwise plated on the electrode making the measurement of limiting currents difficult. In alcoholic solution the limiting current was found to be linear with concentration up to about 0.8 mM hemin.

The log K for reaction 1 found here was 5.11 as compared with 6.34 determined spectrophotometrically without the addition of ethanol.[1] For reaction 2, log K was found to be 0.81 as compared with the literature value of −0.20. The procedure for evaluating the K values was as follows. Polarograms were run on a series of solutions which contained fixed concentrations of hemin (0.8 mM), pyridine (2.0 M), sodium nitrate (1.0 M), and ethanol (30% by volume) but varying concentration of sodium cyanide (10^{-6} to 10^{-1} M). The equilibrium concentration of pyridine was taken as 2.0 M for all calculations. The cyanide ion equilibrium concentration was determined by first subtracting the amount of cyanide present in the hemin species from the total cyanide introduced. The remaining cyanide exists either as HCN or CN^-, the ratio of which can be determined from the known pK_a for HCN and the pH of the solution which varied from 8.6 to 11.2. The concentrations of the hemin species were calculated from the height of the appropriate polarographic wave. This is justified since the diffusion coefficients of all species involved were shown to be essentially equal. Furthermore, the over-all height of the wave(s) remained constant for a given hemin concentration as the cyanide concentration was increased. The differences in equilibrium constants between those found in this work and the previously reported values may be due not only to the presence of ethanol, but also to differences in ionic strength and a small temperature effect. The polarographic method of determining these equilibrium constants has the important advantage that all major species are accounted for since the sum of the limiting currents can be compared with the limiting current of the dipyridine or dicyanide complexes alone.

Hydroxoaquo Complex. The monomeric *trans*-hydroxoaquoprotoporphyrinferrate(III) ion which exists in alkaline ethanolic aqueous solution undergoes a reversible one-electron reduction at a dme in accordance with the equation



$$\left[\begin{array}{l}\text{H}_2\text{O}\\ |\\ \text{Fe}^{\text{III}}\text{–P}\\ |\\ \text{OH}\end{array}\right]^{0} + \text{H}_2\text{O} + e \rightleftharpoons \left[\begin{array}{l}\text{H}_2\text{O}\\ |\\ \text{Fe}^{\text{II}}\text{–P}\\ |\\ \text{H}_2\text{O}\end{array}\right]^{0} + \text{OH}^- \qquad (3)$$

The use of platinum electrodes to study this reaction is precluded, owing to a buildup of reduction product on the electrode. A typical dme polarogram is illustrated in Figure 3. The height of the small wave which pre-

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(17) H. A. Laitinen and L. M. Chambers, *Anal. Chem.*, **36**, 5 (1964).

(18) J. N. Phillips, *Rev. Pure. Appl. Chem.*, **10**, 35 (1960).

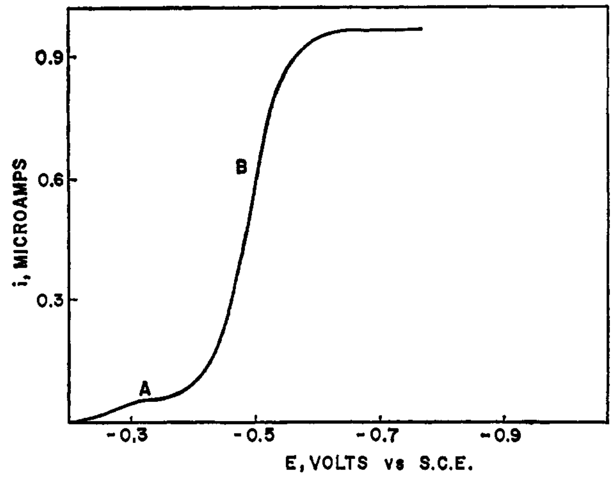

Figure 3. Polarogram of the *trans*-hydroxoaquoprotoporphyrinferrate(III) ion: 0.90 × 10^{-3} M hemin, 0.025 M borax, 30% ethanol, pH 9.5. A, adsorption wave; B, normal wave.

cedes the normal reduction wave is independent of the total hemin concentration and changes in direct proportion with the mercury height. The total diffusion current (sum of the prewave and the normal wave) is proportional to the concentration of hemin. This behavior is characteristic of systems in which the reduction product is strongly adsorbed at the mercury–water interface.[19] For such a system, the true half-wave potential is found at the potential of the half-wave current of the second wave plus a constant value of current corresponding to the height of the adsorption wave.

Equation 3 predicts that the half-wave potential of the hemin species should shift with pH as shown in eq 4.

$$\Delta E_{1/2}/\Delta(\text{pH}) = -0.0591 \qquad (4)$$

This parameter calculated from our data gives a value of −0.058 v/pH unit for the pH range 9.0–12.0. A borate buffer was used in the pH range 9.0–10.5 and a phosphate buffer in the range 10.5–12.0. From the expanded form of the Ilkovič equation,[20] the diffusion coefficient of the monomeric hydroxoaquo species at a total hemin concentration of 1 mM in 30% ethanolic, aqueous solution (pH 9.5) was evaluated as 1.19 × 10^{-6} cm^2/sec. It is interesting to note that this diffusion coefficient is almost an order of magnitude larger than that found in an aqueous solution without alcohol.[5] Experiments in this laboratory confirm this divergence which may possibly be explained by micelle aggregate formation[1] as well as that of dimers.[5]

The adsorption phenomenon observed polarographically is also demonstrated in a rather dramatic way using the technique of cyclic voltammetry with a hanging mercury drop electrode, as shown in Figure 4. On the cathodic sweep one peak is seen, although a small, somewhat ill-defined prewave was noticed on the original oscilloscope photographs if the scale was expanded. Two peak currents are distinguishable on the anodic sweep of this single cycle voltammogram. Brdička has proposed[21] that reduced species adsorbed on the surface of an electrode are in a lower free-energy state than reduced species in solution, and hence are more difficult to oxidize. Tatwawadi and Bard,[16] in their chronopotentiometric study of the adsorption of riboflavin on mercury, found that the "adsorbed layer last" model for the determination of the amount of adsorption gives best agreement with independent electrocapillarity measurements. With these points in mind, we conclude that the peak occurring at the more positive potential on our voltammograms is due to the oxidation of adsorbed material and hence is a measure of the number of molecules adsorbed. On this basis Γ is evaluated as 1.1 × 10^{-10} mole/cm^2, which may be compared with Γ = 1.2 × 10^{-10} mole/cm^2, evaluated from the dme polarogram of Figure 3 by the method of Brdička.[19]

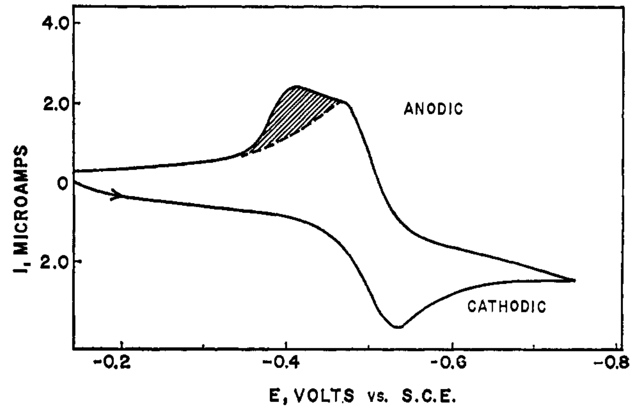

Figure 4. Cyclic voltammogram of the *trans*-hydroxoaquoprotoporphyrinferrate(III) ion: 0.90 × 10^{-3} M hemin, 0.025 M borax, 10% ethanol, pH 9.4; sweep rate, 0.186 v/sec.

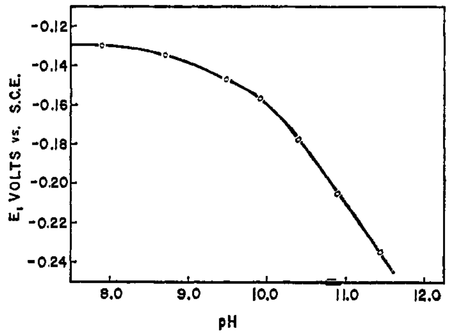

Figure 5. Pyridine hemichrome. Variation of $E_{1/2}$ with pH.

Pyridine Hemichrome at Higher pH Values. In the pH range 7.5–8.3, the pyridine hemichrome is reversibly reduced at an invariant potential using either mercury or platinum electrodes. On the basis of dme data, the diffusion coefficient of the pyridine hemichrome was evaluated as 1.33 × 10^{-6} cm^2/sec using the expanded Ilkovič equation.[20] This assignment applies to a solution which contained 2.24 × 10^{-3} M hemin, 2.5 M pyridine, 30% by volume ethanol, and 1 M $NaNO_3$. Above pH 8.3, the polarographic wave corresponding to the pyridine species shifts cathodically. In the pH range 8.3–10.5, the cathodic shift of $E_{1/2}$ is not linearly related to Δ(pH). Apparently, this pH range involves a transition region in which two or possibly more closely related pyridine–hemin species exist. Above pH 10.5, a linear dependence of half-wave potential upon pH is observed. From pH 10.5 to 12.0 $\Delta E_{1/2}/\Delta(\text{pH})$ has a

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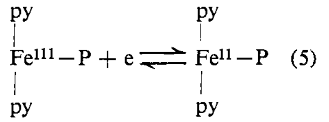
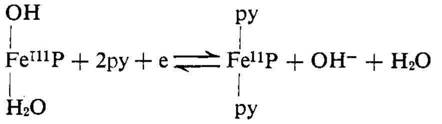
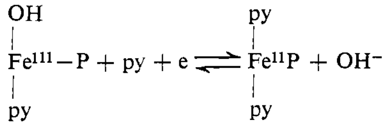
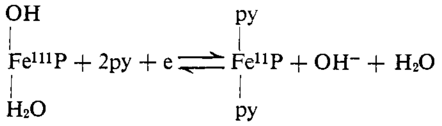
(19) R. Brdička, *Z. Elektrochem.*, **48**, 278 (1942).
(20) I. Koltoff and Izutzu, *J. Am. Chem. Soc.*, **86**, 1275 (1964).
(21) R. Brdicka, *Collection Czech. Chem. Commun.*, **12**, 522 (1947).

Table IV. Electrode Reactions of Iron-Protoporphyrin in Pyridine as a Function of pH

pH range	Reaction responsible for first wave	Reaction responsible for second wave
7.5–8.3	 $\overset{\text{py}}{\underset{\text{py}}{\text{Fe}^{\text{III}}}}\text{–P} + e \rightleftharpoons \overset{\text{py}}{\underset{\text{py}}{\text{Fe}^{\text{II}}}}\text{–P}$ (5)	None
8.3–9	Transition region involving two or more pyridine-hemin species	None
9–10.5	Transition region involving two or more pyridine-hemin species	 $\overset{\text{OH}}{\underset{\text{H}_2\text{O}}{\text{Fe}^{\text{III}}}}\text{P} + 2\text{py} + e \rightleftharpoons \overset{\text{py}}{\underset{\text{py}}{\text{Fe}^{\text{II}}}}\text{P} + \text{OH}^- + \text{H}_2\text{O}$ (6)
10.5–12.0	 $\overset{\text{OH}}{\underset{\text{py}}{\text{Fe}^{\text{III}}}}\text{–P} + \text{py} + e \rightleftharpoons \overset{\text{py}}{\underset{\text{py}}{\text{Fe}^{\text{II}}}}\text{P} + \text{OH}^-$ (7)	 $\overset{\text{OH}}{\underset{\text{H}_2\text{O}}{\text{Fe}^{\text{III}}}}\text{P} + 2\text{py} + e \rightleftharpoons \overset{\text{py}}{\underset{\text{py}}{\text{Fe}^{\text{II}}}}\text{P} + \text{OH}^- + \text{H}_2\text{O}$

value of 0.060 v/pH unit. The dependency of $E_{1/2}$ upon pH is illustrated in Figure 5.

Furthermore, solutions of pH 9 and higher exhibit a second well-defined polarographic wave (in the range -0.3 to -0.45 v *vs.* sce) as shown in Figure 6. This second wave shifts cathodically with a linear dependence of $E_{1/2}$ upon pH; $\Delta E_{1/2}/\Delta(\text{pH}) = -0.060$. As the pH of a given solution is increased, the height of the first wave decreases in size while the height of the second wave increases. Plots for both waves of log $[(i_d - i)/i]$ *vs.* E were found to be linear and to have a slope of 0.060, thus indicating that both reactions are reversible, one-electron reductions. Cyclic voltammetry was useful in identifying reduction products. It turns out that all of the various iron(III) species have a common reduction product, *i.e.*, pyridine hemochrome (Figure 7).

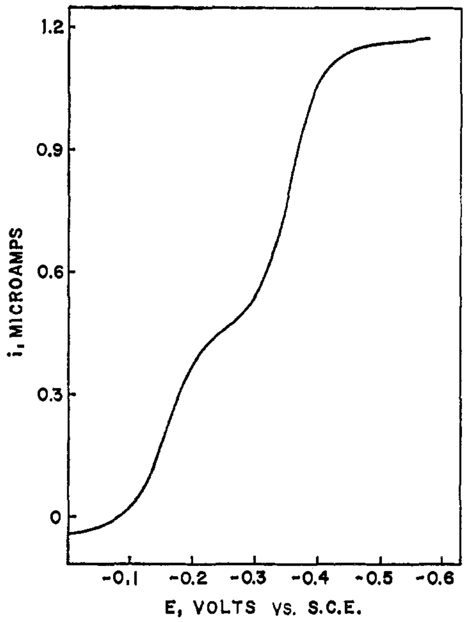
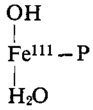
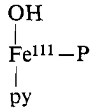


Figure 6. Polarogram of pyridine hemichrome at pH 10.0: 0.98×10^{-3} *M* hemin, 0.025 *M* borax, 2.5 *M* pyridine, 10% ethanol.

Conclusions derived from the above observations are summarized in Table IV. The first wave in Figure 6 corresponds to reaction 7 and the second wave to reaction 6. These formulations are consistent with the current knowledge of the chemistry of iron-protoporphyrin complexes.[3] That all species proposed are monomers is indicated by the fact that the over-all diffusion current remains essentially constant throughout the pH range studied, and the diffusion coefficients found are substantially higher than those previously found for dimers.[5] The exact nature of the species designated A or possibly B may be in some doubt


$\overset{\text{OH}}{\underset{\text{H}_2\text{O}}{\text{Fe}^{\text{III}}}}\text{–P}$

A


$\overset{\text{OH}}{\underset{\text{py}}{\text{Fe}^{\text{III}}}}\text{–P}$

B

since these formulations, while consistent with the electrochemical data, do not show why one is transformed into the other as the pH is increased. Weak aggregates or complexes containing more than two ligands in addition to the porphyrin have been cited as the causes of similar anomalies.

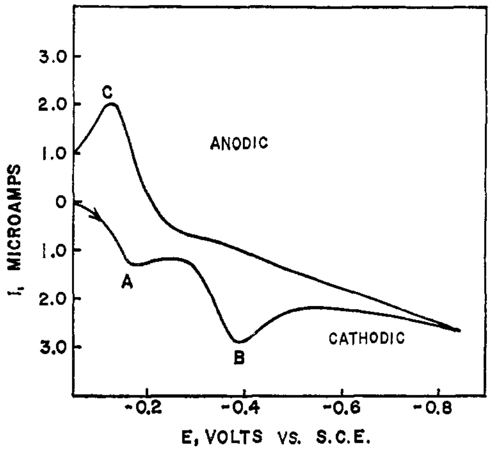
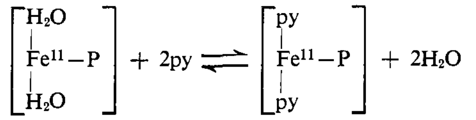


Figure 7. Cyclic voltammogram of pyridine hemichrome at pH 10.2 (one cycle only): 0.86×10^{-3} *M* hemin, 0.1 *M* $NaHCO_3$, 2.0 *M* pyridine, 30% ethanol. A, reduction of pyridine hemichrome; B, reduction of hydroxoaquo complex; C, oxidation of pyridine hemochrome; scan rate = 0.129 v/sec.

It is to be noted by comparing eq 3 and 6 that the product resulting from the reduction of the hydroxoaquo complex depends on the solution composition, *i.e.*, the reduction product in pyridine solution, is the pyridine hemochrome whereas, in the absence of pyridine, the *trans*-diaquoprotoporphyrinferrate(II) ion is formed. Cyclic voltammetry indicates that the ligand-exchange reaction

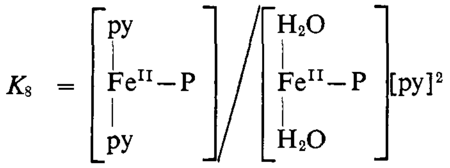


$$\left[\begin{array}{l} H_2O \\ | \\ Fe^{II}-P \\ | \\ H_2O \end{array}\right] + 2py \rightleftharpoons \left[\begin{array}{l} py \\ | \\ Fe^{II}-P \\ | \\ py \end{array}\right] + 2H_2O \qquad (8)$$

is very fast. Under these circumstances, it is possible to develop, by conventional means, a thermodynamic equation relating the change in $E_{1/2}$ due to the different electrode reactions to K_8, the equilibrium constant for reaction 8. Equation 9 defines this relationship where the $E_{1/2}$ values refer to potentials obtained for reactions 3 and 6 at the same pH.

$$(E_{1/2})_6 - (E_{1/2})_3 = 0.0591 \log K_8 \qquad (9)$$

where



$$K_8 = \left[\begin{array}{l} py \\ | \\ Fe^{II}-P \\ | \\ py \end{array}\right] \Bigg/ \left[\begin{array}{l} H_2O \\ | \\ Fe^{II}-P \\ | \\ H_2O \end{array}\right] [py]^2$$

Log K_8 was evaluated as 2.87 ± 0.05 from data taken at five different pH values. A value of log $K = 5.0$ for reaction 8 in 2.5% cetyltrimethylammonium bromide aqueous solution has been reported.[3]

A study of some of the rates of displacement of one ligand by another with complexes of this type is now underway in this laboratory.

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Polarographic Kinetic Currents in Mixtures of Persulfate and Copper(II) in Chloride Medium[1]

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Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, and the Chemistry Department, University of Melbourne, Parkville N.2, Victoria, Australia. *Received November 4, 1965*

Abstract: The polarographic reduction of mixtures of copper and persulfate in 0.1 or 1 *M* chloride medium yields two waves. The second diffusion current is the sum of the Cu(II) → Cu(0) and persulfate reductions. The first wave is interpreted as the sum of the Cu(II) → Cu(I) wave and a kinetic current due to reaction of the copper(I) formed at the electrode with persulfate. The rate constant for the reaction was determined to be 1.4×10^3 l. mole^{-1} sec^{-1} at 25°. Reduction of persulfate at the electrode at potentials corresponding to the first wave is postulated to be completely suppressed by the adsorption of copper(I) chloride complex. Cuprous thiocyanate, adsorbed in a monomolecular layer, completely suppresses persulfate reduction at the dme.

Persulfate yields a reduction wave at the dropping mercury electrode (dme) which starts at the potential of anodic dissolution of mercury. The persulfate current–potential curve exhibits certain anomalous characteristics under various conditions, this being a common feature of the electroreduction of multivalent anions.[2] Krjukova[3] found a minimum on the persulfate wave, the decrease commencing at potentials more negative than the electrocapillary maximum. The decrease is dependent on the nature and concentration of supporting electrolyte and is due to electrostatic repulsion of the persulfate ion by the negatively charged electrode surface. This repulsion can be eliminated by the adsorption of capillary active cations of the type NR_4^+.[4]

The reduction of persulfate at a positively charged electrode surface can be inhibited by the adsorption of anions, the inhibiting action increasing with increase in the adsorbability of the anion.[5,6] This inhibiting action increases greatly in the presence of surface-active cations of the type NR_4^+, resulting in minima on the current–potential curve.[4] Kolthoff and Okinaka[7] found that the formation of an insoluble film of mercurous iodide depresses the persulfate diffusion current considerably, concentrations of iodide as low as 10^{-4} *M* being effective; the film behaves like a negatively charged surface-active substance. A similar decrease was observed in the presence of mercurous bromide.

The polarographic reduction of copper(II) in chloride medium occurs in two steps, Cu(II) → Cu(I) and Cu(I) → Cu(0), producing a double wave.[8] The present

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[1] This investigation was carried out under a grant from the National Science Foundation in Minnesota and a Research Fellowship in Melbourne.

[2] A. N. Frunkin and N. Nikolaeva-Fedorovich, *Progr. Polaro.*, **1**, 223 (1962).

[3] T. A. Krjukova, *Dokl. Akad. Nauk SSSR*, **65**, 517 (1949).

[4] A. N. Frumkin, "Proceedings of the 2nd International Congress on Surface Activity, Electrical Phenomena," Butterworths, London, 1957, p 58.

[5] T. Kalish and A. Frumkin, *Zh. Fiz. Khim.*, **28**, 473 (1954).

[6] A. Frumkin, N. Nikolaeva-Fedorovich, and R. Ivanova, *Can. J. Chem.*, **37**, 253 (1959).

[7] I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **83**, 47 (1961).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers Inc., New York, N. Y., 1952, p 493.