Table I. Comparison of the ARDF's of the Aqueous ICHH Solutions 10.4-A and 10.4-B

	$g(r)$			$g(r)$	
r, Å	10.4-A	10.4-B	r, Å	10.4-A	10.4-B
0.1	0.01	0.01	2.6	0.57	0.62
0.2	0.04	0.00	2.7	0.68	0.81
0.3	0.08	−0.05	2.8	0.81	0.99
0.4	0.06	−0.07	2.9	0.97	1.13
0.5	−0.01	−0.08	3.0	1.13	1.14
0.6	−0.03	−0.05	3.1	1.19	1.20
0.7	−0.04	−0.03	3.2	1.09	1.14
0.8	−0.01	0.03	3.3	0.89	1.02
0.9	0.03	0.06	3.4	0.84	0.90
1.0	0.01	0.03	3.5	0.80	0.86
1.1	−0.05	−0.01	3.6	0.86	0.84
1.2	−0.09	−0.03	3.7	0.96	0.87
1.3	−0.06	−0.04	3.8	1.19	0.93
1.4	−0.03	0.02	3.9	1.41	1.07
1.5	0.04	0.05	4.0	1.44	1.27
1.6	0.19	−0.02	4.1	1.30	1.44
1.7	0.37	−0.04	4.2	1.08	1.47
1.8	0.70	0.30	4.3	0.87	1.38
1.9	1.09	0.97	4.4	0.74	1.11
2.0	1.31	1.62	4.5	0.71	0.80
2.1	1.24	2.03	4.6	0.79	0.60
2.2	0.98	1.83	4.7	0.87	0.58
2.3	0.69	1.27	4.8	0.97	0.71
2.4	0.52	0.69	4.9	1.07	0.87
2.5	0.50	0.45	5.0	1.15	0.99

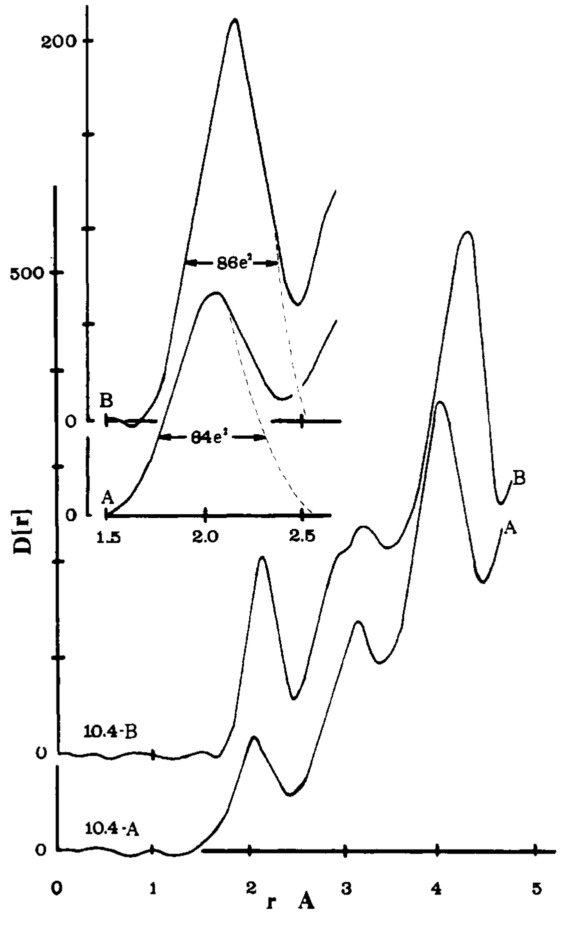


Figure 1. ARDF's calculated with a dampening factor of $\exp(-0.01s^2)$ for the 10.4 *m* aqueous solution prepared from $FeCl_3{\cdot}6H_2O$ obtained 2–6 weeks (10.4–A) and 14–15 months (10.4–B) after solution preparation. In the insert the resolution of and the area under the primary peak in each $D(r)$ are shown.

Although the average specie found in this solution is somewhat similar to that reported by Magini and Radnai[4] to exist in one of their solutions, our findings should *not* be taken as evidence to support the existence of any of the several solute species they propose. Rather, this reinvestigation establishes that hexaaquoiron(III) is the initial product formed when $FeCl_3{\cdot}6H_2O$ is dissolved into water and that Fe^{3+} appears to be, on the average, octahedrally coordinated in this solution even though, after 14 months, some of the inner-sphere waters have been replaced by chlorides.

Registry No. $FeCl_3{\cdot}6H_2O$, 10025-77-1; $[Fe(OH_2)_6]Cl_3$, 57533-67-2.

Contribution from the Laboratoire de Chimie de l'Ecole
Normale Supérieure, Associé au CNRS,
75231 Paris Cedex 05, France

Formation of a Complex with a Carbide Bridge between Two Iron Atoms from the Reaction of (Tetraphenylporphyrin)iron(II) with Carbon Tetraiodide

Daniel Mansuy,* Jean-Pierre Lecomte, Jean-Claude Chottard, and Jean-François Bartoli

Received December 17, 1980

Dihalogenocarbene complexes of iron porphyrins, Fe(porphyrin)(CXX′) with X = X′ = F, Cl, or Br, have recently been obtained from reaction of tetrahalomethanes with iron porphyrins in the presence of an excess of reducing agent[1-3] (eq 1). These complexes could be good precursors of other organometallic species such as other carbene or carbyne complexes, if it were possible to use the leaving-group properties of the halogen substituents of their carbenic carbon. Effectively, the $Fe(TPP)(CBr_2)$ complex is more reactive toward nucleophiles than the $Fe(TPP)(CCl_2)$ complex.[3,4] Therefore we have attempted to prepare the $Fe(TPP)(CI_2)$ complex from the reaction between CI_4 and Fe(TPP) in the presence of a reducing agent in excess. This note reports that this reaction does not afford the expected complex but leads to a new complex which exhibits characteristics corresponding to a heme dimer structure with two iron atoms bridged by a formally dicarbenic carbon. Quite independently of our work, it has been very recently predicted[5] from calculations that the complex $[Fe(TPP)]_2C$ should be a stable diamagnetic molecule with a linear M–C–M spine.

$$\mathrm{Fe^{II}(P)} + \mathrm{CX_3X'} \xrightarrow[-2X^-]{+2e^-} [\mathrm{(P)Fe^{II}} \leftarrow \mathrm{CXX'}] \tag{1}$$

Experimental Section

Preparation of $[Fe(TPP)]_2C$ (1). $Fe^{III}(TPP)(Cl)$ (500 mg, 6.9×10^{-4} mol) was dissolved in 25 mL of an anaerobic (argon) 9:1(v:v) CH_2Cl_2–CH_3OH solution, in the presence of 100 mg of iron powder, in a tube stoppered with a serum cap. CI_4 (360 mg, 6.9×10^{-4} mol) was then added under argon and the solution vigorously stirred at 20 °C. Formation of **1** is complete within about 1 h under these conditions, as shown by visible spectroscopy (λ_m = 400 and 530 nm). After filtration of the solution, washing with water, drying over Na_2SO_4, and evaporation, the solid residue was dissolved in a 1:9 (v:v) CH_2Cl_2–CH_3OH (or C_2H_5OH) solution. Complex **1** was then ob-

---

(1) Mansuy, D.; Lange, M.; Chottard, J. C.; Guérin, P.; Morlière, P.; Brault, D.; Rougee, M. *J. Chem. Soc., Chem. Commun.* **1977**, 648.

(2) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F.; Chevrier, B.; Weiss, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 781.

(3) Mansuy, D. *Pure Appl. Chem.* **1980**, *52*, 681.

(4) TPP is used for the dianon of *meso*-tetraphenylporphyrin, DMF for dimethylformamide.

(5) Tatsumi, K.; Hoffman, R.; Whangbo, M. H. *J. Chem. Soc., Chem. Commun.* **1980**, 509.

0020-1669/81/1320-3119$01.25/0 © 1981 American Chemical Society

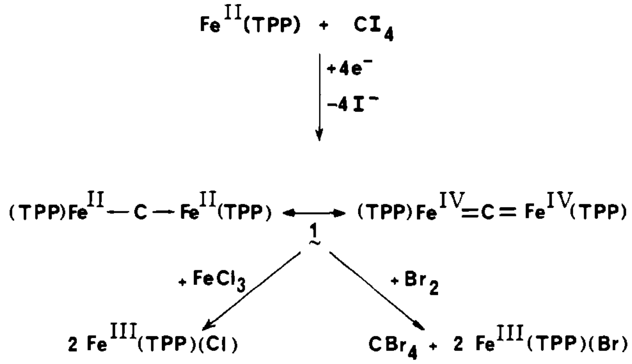
tained as a purple powder [450 mg, yield ≃ 90%, single spot in thin-layer chromatography on silica gel with C_6H_6–CH_2Cl_2 (80:20)]. Column chromatography on silica gel [eluant cyclohexane–benzene (8:2)] can be used to get highly purified samples. For vapor pressure osmometry measurements, lyophilization of the purple powder, after dissolution in benzene, was done.

Results and Discussion

Reaction of 5 mM Fe(TPP) in CH_2Cl_2–CH_3OH (9:1) with CI_4 (1 equiv) in the presence of an excess of iron powder, with vigorous stirring under argon at room temperature, leads quantitatively, after about 2 h, to a new complex, **1**. This complex can be equally obtained from reaction of Fe(TPP) with CI_4 in C_6H_6 in the presence of excess aqueous sodium dithionite. It exhibits a visible spectrum (in C_6H_6), with two peaks at 400 and 530 nm, which is different from the spectrum (410 and 525 nm) characteristic of the various Fe(TPP)(CXX′) complexes prepared previously from polyhalomethanes under identical conditions.[1-3]

Molecular weight measurements (vapor pressure osmometry in $CHCl_3$ at 38 °C) substantiate a dinuclear formulation for complex **1** with $M_r = 1350 \pm 40$ determined at a concentration of 8 g/L.[6] No molecular association seems to occur in this solvent since one does not observe any significant variation of the molecular weight upon variation of the concentration of the complex from 2 to 8 g/L. Moreover, the visible spectrum of complex **1** (in C_6H_6) does not change when its concentration varies from 10^{-6} to 10^{-4} M. Its IR spectrum (KBr) exhibits two bands at 940 (vs, br) and 883 cm^{-1} (m, sh) which do not appear in the spectra of the Fe^{III}(TPP)(Cl) and Fe(TPP)(CCl_2) complexes.[2] Analogous bands have been reported for the heme dimer complexes $[Fe(TPP)]_2O$ [885 (m), 870 cm^{-1} (vs)] and $[Fe(TPP)]_2N$ [910 (vs), 885 cm^{-1} (m)].[7,8] They are believed to correspond to the asymetric Fe–X–Fe stretch (X = O or N). Except for these two bands, the IR spectrum of complex **1** is very similar to those of $[Fe(TPP)]_2O$ and $[Fe(TPP)]_2N$. These results suggest the formulation $[Fe(TPP)]_2C$ for complex **1**. Its characteristics are in agreement with those for a heme dimer structure with an unsubstituted carbon atom bridging the two iron atoms, as follows. (a) Its mass spectrum (field desorption) shows a molecular peak at *m/e* 1348,[6] the major peak at *m/e* 668 corresponding to Fe(TPP). (b) Treatment of complex **1** by oxidants such as $FeCl_3$ or $CuCl_2$ leads to a quantitative yield of Fe^{III}(TPP)(Cl), showing that the porphyrin ring is not irreversibly altered upon formation of complex 1 from Fe(TPP). (c) The elemental analysis (C, H, N)[9] of a sample of the complex containing 2 mol of H_2O of crystallization (as determined by ^1H NMR) is in agreement with the formula $[Fe(TPP)]_2C{\cdot}2H_2O$. (d) Its magnetic susceptibility, $\mu_{eff} = 0$,[10] is indicative of a low-spin Fe^{II} structure, which is confirmed by the positions and shapes of the signals of its ^1H NMR spectrum[11] ($CDCl_3$, Me_4Si, ppm) as follows: 8.4 (4 H, m), 8.36 (8 H, s), 7.79 (8 H, m), 7.5 (8 H, m). The presence of a sharp singlet for the pyrrolic protons is indicative of an axial symmetry. (e) Upon treatment at 25 °C of complex **1** by 4 equiv of Br_2, a quantitative yield of CBr_4 and Fe^{III}(TPP)(Br) is obtained (Scheme I). (f) Complex **1** is formed with more than 80% yield by reaction of CI_4 with Fe(TPP) with use of the molar proportions 1:2 in the presence of iron powder in excess.

Scheme I



According to the proposed structure (TPP)FeCFe(TPP) for complex **1**, it is the carbon analogue of the dimeric $[Fe(TPP)]_2O$[7] and $[Fe(TPP)]_2N$[8] complexes. The X-ray structure of the $[Fe(TPP)]_2O$ complex[7b] shows that the mean planes of the two porphinato cores are separated by ~5.2 Å and that the iron atoms are displaced 0.5 Å from the mean plane of the porphinato cores toward the axial oxygen ligand. These characteristics reflect the steric constraints due to the proximity of the bulky phenyl substituents of the two porphyrins. One should expect these steric constraints to be more important or at least similar in complex **1**. This is effectively indicated by the following ^1H and ^{13}C NMR data and chemical properties of complex **1**.

Its ^{13}C NMR spectrum ($CDCl_3$, Bruker 90 MHz, Me_4Si) exhibits eight peaks at 145, 141.3, 134.7, 134.4, 131.2, 126.9, 126.1, and 120.5 ppm for the porphyrin carbons.[12] It is very similar to those of Zn(TPP)[13] and Fe(TPP)(CCl_2)[1] except for the phenyl ring signals which, instead of one sharp singlet for the ortho carbons and an other one for the meta carbons, respectively appear as the two 134.4 and 134.7 ppm singlets (each integrating for four carbons) and the broad 126.9 ppm singlet (eight carbons). While rotation of the phenyl rings is rapid vs. the NMR time scale in Zn(TPP) or Fe(TPP)(CCl_2), these results are indicative of a slower rotation in the case of complex **1**. The ^1H NMR spectrum of complex **1** at 20 °C in C_6D_6 (Cameca 250 MHz) shows, in addition to the pyrrolic protons singlet at 8.6 ppm, two doublets[14a] at 8.67 and 7.58 [J = 7.5Hz, 2 × 4 H (phenyl ortho and ortho′ H)] and three triplets at 7.82, 7.4, and 7.63 ppm [J = 7.5 Hz, 3 × 4 H (respectively, phenyl meta, meta′, and para H[14b])], also indicating a slow (or blocked) rotation of the phenyl rings at this temperature.[14c]

Complex **1** exhibits chemical properties very different from those of the Fe(TPP)(CCl_2) or Fe(TPP)(CBr_2) complexes. First, it is stable for weeks to dioxygen either in the solid state or in aerated C_6H_6 or CH_2Cl_2, whereas Fe(TPP)(CCl_2) has a half-life of about 4 h in aerated benzene.[1] Second, its iron–carbon bonds are stable in the presence of 1 M primary amines RNH_2 such as isopropyl- or *n*-butylamine, conditions

---

(6) Calculated for $[Fe(TPP)]_2C$: $M_r = 1348$.

(7) (a) Cohen, I. A. *J. Am. Chem. Soc.* **1969**, *91*, 1980. (b) Hoffman, A. B.; Collins, D. M.; Day, V. W.; Fleischer, E. B.; Srivastava, T. S.; Hoard, J. L. *Ibid.* **1972**, *94*, 3620. (c) La Mar, G. N.; Eaton, G. R.; Holm, R. H.; Walker, F. A. *Ibid.* **1973**, *95*, 63. (d) Torrens, M. A.; Straub, D. K.; Epstein, L. M. *Ibid.* **1972**, *94*, 4160.

(8) (a) Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 1747. (b) Scheidt, W. R.; Summerville, D. A.; Cohen, I. A. *J. Am. Chem. Soc.* **1976**, *98*, 6623.

(9) Anal. Calcd for $[Fe(TPP)]_2C{\cdot}2H_2O$: C, 77.2; H, 4.05; N, 8.09. Found: C, 77.04; H, 4.16; N, 8.01.

(10) Measured at 33 °C by the Evans method: Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(11) Del Gaudio, J.; La Mar, G. N. *J. Am. Chem. Soc.* **1978**, *100*, 1112.

(12) The resonance of the axial carbon ligand could not be detected. This has been previously encountered with such quaternary carbons far from any proton.[1,17]

(13) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1976**, *15*, 134.

(14) (a) The phenyl protons appear as doublets or triplets because the resolution is not sufficient to take into account the small J_4. (b) The assignment of phenyl meta and para protons is based upon double resonance data. (c) At 110 °C in $CDCl_2$–$CDCl_2$, the eight meta and four para phenyl protons of complex **1** appear as a unique broad signal (as this is the case for Fe(TPP)(CCl_2) or Fe(TPP)(CS) at 20 °C) and the signals of the ortho and ortho′ phenyl protons are at coalescence. More precise determinations are difficult since complex **1** begins to decompose at this temperature.

under which $Fe(TPP)(CCl_2)$ and $Fe(TPP)(CBr_2)$ are completely transformed into $Fe(TPP)(CNR)(RNH_2)$ within a few seconds.[3,15] Similarly, complex **1** is half-transformed into the hemochrome $Fe(TPP)(pyridine)_2$, after a ~15 h reaction with 1 M pyridine in benzene at 25 °C, conditions in which $Fe(TPP)(CBr_2)$ is half-transformed after about 2 min.[3]

Another unique property of complex **1** compared to other $Fe^{II}(TPP)$ pentacoordinated complexes such as $Fe(TPP)(CCl_2)$,[1] $Fe(TPP)(CS)$,[16] or $Fe(TPP)(C{=}C(p\text{-}ClC_6H_4)_2)$[17] is its very low binding affinity for various ligands. Oxygen-containing ligands such as CH_3OH or DMF do not bind to complex **1** since its visible spectra in C_6H_6, DMF, or C_6H_6–CH_3OH (90:10) are identical.[18] The addition of pyridine or isopropylamine to complex **1** (in C_6H_6) leads immediately to the formation of new entities characterized respectively by peaks at 418 (ϵ 3 × 10^5), 532 (ϵ 12 × 10^3) and 560 nm (ϵ 11 × 10^3), and 418 (ϵ 2.9 × 10^5), 535 (ϵ 12 × 10^3) and 561 nm (ϵ 11 × 10^3). Their formation constants at 27 °C are ~75 and 50 L·mol^{-1}, whereas the formation constants of the hexacoordinated complexes $Fe(TPP)(CCl_2)(py)$ or $Fe(TPP)(CS)(py)$ from the corresponding pentacoordinated complexes and pyridine are, respectively 3500[1] and 5600 L mol^{-1}.[16]

All these results are in agreement with the (TPP)FeCFe(TPP) structure for complex **1** involving a central carbon atom hardly accessible to reactants and iron atoms greatly displaced from the mean porphyrin plane and hardly able to bind ligands. Complex **1** would be, to our knowledge, the first example of a transition-metal complex of the type M=C=M[19] involving a formally dicarbenic carbon atom ligand bridging two transition metals.

Acknowledgment. We are grateful to Dr. P. Battoni and M. Lange for helpful suggestions.

Registry No. 1, 75249-87-5; $Fe^{III}(TPP)(Cl)$, 16456-81-8; CI_4, 507-25-5.

---

(15) Mansuy, D.; Lange, M.; Chottard, J. C.; Bartoli, J. F. *Tetrahedron Lett.* **1978**, *33*, 3027.

(16) Mansuy, D.; Battioni, J. P.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4311.

(17) Mansuy, D.; Lange, M.; Chottard, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 3213.

(18) For comparison, the association constants of DMF or alcohols to $Fe(TPP)(CCl_2)^2$ are ~5 L mol^{-1}.

(19) Very recently, the complex $Sn(TPP)(CRe(CO)_3)_2$ involving two Sn–C–Re bonds has been reported: Noda, I.; Kato, S.; Mizuta, M.; Yasuoka, N; Kasai, N. *Angew. Chem., Int. Ed., Engl.* **1979**, *18*, 83. It is noteworthy that various carbido carbonyl clusters such as $Fe_5(CO)_{15}C$, $Ru_6(CO)_{17}C$, and $Co_6(C)(CO)_{12}S_2$ have been described: Braye, E. H.; Dahl, L. F.; Hübel, W.; Wampler, D. L. *J. Am. Chem. Soc.* **1962**, *84*, 4633. Johnson, B. F. G.; Jonston, R. D.; Lewis, J. *Chem. Commun.* **1967**, 1057. Bor, G.; Gervasio, G.; Rossetti, R.; Stanghallini, P. L. *J. Chem. Soc., Chem. Commun.* **1978**, 841. Tachikawa, M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 4541.

Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Simple Electrochemical Approach for Determining Rapid Homogeneous Redox Reaction Rate Constants

Tomislav Matusinovic and Donald E. Smith*

Received December 17, 1980

We recently have developed a novel electrochemical procedure for measuring rapid irreversible homogeneous redox reaction rates.[1-5] The method is applied readily to inorganic and organometallic redox processes. It is applicable to second-order rate constants in the range normally probed by stopped-flow and pulsed radiolysis. We view the electrochemical approach as complementary to these more conventional procedures in most cases, and, with certain systems, it may prove to be the preferred or only method available. The latter remark is based on the fact that the electrochemical approach does not require an absorption or emission spectrum. Consequently, difficulties attending the lack of a spectroscopic response or a complex overlapping multicomponent spectra do not influence the electrochemical procedure. It shares with pulsed radiolysis the advantage over stopped flow that highly air-sensitive compounds are prepared in situ rather than in bulk quantities.

Table I. Diffusion Coefficient Values Determined for Various Relevant Ions with Use of Polarography and Eq 1[a]

ionic species	diffusion coeff, cm^2 s^{-1} × 10^6
Eu(III)	7.88
RN_3^{2+}	5.08
RNO_3^{2+}	5.16
$RNCS^{2+}$	1.46
$RONO^{2+}$	3.40
RNO_2^{2+}	6.01
RPO_4	1.88

[a] Solvent medium was a pH 0.3 aqueous electrolyte containing $NaClO_4$ and $HClO_4$ of 1 M ionic strength. R = $Co(NH_3)_5^{3+}$.

The method is based on the electrode reaction mechanism

$$A + e^- \rightleftharpoons B \text{ (electrode reaction } E_1^\circ, E_{1/2,1})$$

$$C + e^- \rightleftharpoons D \text{ (electrode reaction, } E_2^\circ, E_{1/2,2}) \qquad \text{(R1)}$$

$$A + D \xrightarrow{k_{2nd}} B + C \text{ (homogeneous redox reaction)}$$

where $E_1^\circ >> E_2^\circ$ and $E_{1/2,1} >> E_{1/2,2}$ (E_i° and $E_{1/2,i}$ represent standard potentials and observed dc polarographic half-wave potentials, respectively). A specific example is

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \; (E_1^\circ, E_{1/2,1})$$

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \; (E_2^\circ, E_{1/2,2})$$

$$Fe^{3+} + Cr^{2+} \xrightarrow{k_{2nd}} Fe^{2+} + Cr^{3+}$$

Basically, one is dealing with two independent electrode reactions coupled by a homogeneous redox reaction. A classical example of such a mechanism is the so-called catalytic wave,[6] whose properties have been used for many years to deduce homogeneous redox reaction rate data. However, such processes are infrequently encountered because of the nonthermodynamic requirement that for $E_1^\circ >> E_2^\circ$ one must have $E_{1/2,1} << E_{1/2,2}$ or vice versa. However, Mechanism R1 requires that the order of the observed half-wave potentials be the same as the standard potentials, a condition representing the vast majority of such two-component systems. Although complicated in its derivation, the rate law for the reaction sequence give above[1] predicts that a very simple experimental procedure may be applied to obtain the rate constant for the homogeneous redox reaction. One simply obtains ac polarograms of the more difficultly reduced component (e.g., Cr^{3+}) in the absence and presence of the more easily reduced substance (e.g., Fe^{3+}). One then plots as a function of the applied dc potential the *ratio* of the ac current in the presence of the more easily reduced substance over the corresponding current

---

(1) Ruzić, I.; Smith, D. E.; Feldberg, S. W. *J. Electroanal. Chem.* **1974**, *52*, 157.

(2) Schwall, R. J.; Ruzić, I.; Smith, D. E. *J. Electroanal. Chem.* **1975**, *60*, 117.

(3) Schwall, R. J.; Smith, D. E. *J. Electroanal. Chem.* **1978**, *94*, 227.

(4) Schwall, R. J.; Doctoral Disseration, Northwestern University, Evanston, IL, 1977.

(5) Matusinovic, T.; Smith, D. E. *J. Electroanal. Chem.* **1979**, *98*, 133.

(6) Heyrovsky, J.; Kuta, J. "Principles of Polarography"; Academic Press: New York, 1966; pp 380-392.

0020-1669/81/1320-3121$01.25/0 © 1981 American Chemical Society