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OPTICAL AND ELECTROCHEMICAL STUDIES OF ADSORBED TRANSITION META--ETC(U)

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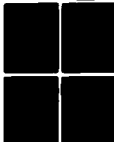
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Task No. NR 359-451

LEWIS

9 TECHNICAL REPORT No. 49

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Optical and Electrochemical Studies of Adsorbed Transition

Metal Complexes and Their <sup>M</sup> Electrochemical Properties

by

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E. Yeager, José Zagal, B. Z. Nikolic and R. R. Adzic

Prepared for Presentation

at the

14 TR-49

Third Symposium on Electrode Processes  
National Meeting, The Electrochemical Society  
Boston, Massachusetts - May 6-11, 1979

12 30

Case Laboratories for Electrochemical Studies  
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER 49	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) Optical and Electrochemical Studies of Adsorbed Transition Metal Complexes and their O <sub>2</sub> Electro- catalytic Properties		5. TYPE OF REPORT & PERIOD COVERED Technical Report #49	
7. AUTHOR(s) E. Yeager, José Zagal, B.Z. Nikolic and R.R. Adzic		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. of Chemistry Case Western Reserve University Cleveland, Ohio 44106		8. CONTRACT OR GRANT NUMBER(s) N00014-75C-0953	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Program - Chemistry Code 472 Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-451	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 1 May 1979	
		13. NUMBER OF PAGES 20	
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Oxygen electrochemistry, electrocatalysis, transition metal macrocyclics, electrosorption, spectroelectrochemistry			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Water soluble transition metal macrocyclics such as the tetrasulfonated phthalo- cyanines (TSPC) are strongly adsorbed on noble metal and graphite electrodes in acid and alkaline electrolytes. The CoTSPC is a good catalyst for O <sub>2</sub> reduction to peroxide and the FeTSPC for the overall 4-electron reduction. The optical proper- ties of the adsorbed species have been examined using reflectance spectroscopy and evidence obtained for the O <sub>2</sub> adduct with the adsorbed complexes. ↩			

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OPTICAL AND ELECTROCHEMICAL STUDIES OF ADSORBED  
TRANSITION METAL COMPLEXES AND THEIR O<sub>2</sub>  
ELECTROCATALYTIC PROPERTIES

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ABSTRACT

Water soluble transition metal macrocyclics such as the tetrasulfonated phthalocyanines (TSPC) are strongly adsorbed on noble metal and graphite electrodes in acid and alkaline electrolytes. The CoTSPC is a good catalyst for O<sub>2</sub> reduction to peroxide and the FeTSPC for the overall 4-electron reduction. The optical properties of the adsorbed species have been examined using reflectance spectroscopy and evidence obtained for the O<sub>2</sub> adduct with the adsorbed complexes.

I. INTRODUCTION

The reduction of O<sub>2</sub> at an electrode surface requires a strong interaction of the O<sub>2</sub> molecule with the electrode surface for the reaction to proceed at substantial rates at reasonable potentials (1). One means for obtaining such strong interactions is through the use of transition metal complexes which form O<sub>2</sub> adducts. Various means are available for chemically binding such complexes to stable electrode surfaces. A particularly attractive approach is the in situ adsorption of the complex onto the surface. Water soluble transition metal macrocyclics such as the tetrasulfonated phthalocyanines (TSP) are strongly adsorbed at monolayer levels on metals such as Au and Pt and on graphite electrodes in acid and alkaline electrolytes (1-4).

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This paper describes electrochemical studies of the cobalt iron tetrasulfonated phthalocyanines adsorbed on graphite and their catalytic properties for  $O_2$  reduction. The electrochemical studies have been complemented with optical specular reflectance measurements of the adsorbed complexes.

## II. $O_2$ INTERACTIONS WITH TRANSITION METAL MACROCYCLIC COMPLEXES

The bonding of  $O_2$  to the transition metal in a macrocyclic complex can involve either lateral or end-on interactions. The Griffiths model (5) (Fig. 1) involves a lateral interaction of the  $\pi$ -orbitals of the  $O_2$  with empty  $d_{z^2}$  orbitals of the transition element with back-bonding from at least partially filled  $d_{xz}$  or  $d_{yz}$  orbitals of the transition element to the  $\pi^*$  orbitals of the  $O_2$ . The Vaska complexes (e.g.,  $Ir(O_2)Cl(CO)(PPh_3)_2$ ) appear to form such complexes with  $O_2$  (6,7). These compounds are selective oxidation catalysts for cyclic olefins (8). The strong metal-to-oxygen interaction results in a weakening and lengthening of the O-O bond. Sufficiently strong interaction may lead to the dissociative adsorption of  $O_2$  with probably simultaneous proton addition and valency change of the transition element in the manner represented by Pathway I in Fig. 3, followed by reduction of the  $M(OH)_2$  to regenerate the catalyst site. Sandstede *et al.* (9-11) have attempted to explain oxygen reduction with square pyramidal Co(II), Fe(II) and Fe(III) complexes on the basis of such  $\pi$  bonding.

With most transition metal complexes the more probable structure for  $O_2$  bonding is the end-on interaction proposed by Pauling (13). The  $\sigma$ -bonding (Fig. 2) can occur through transfer of a metal  $d_{z^2}$  electron to the  $\pi^*$  antibonding  $O_2$  molecular orbital with possible retrodonative bonding from  $O_2$   $\pi$  orbitals to metal d orbitals (14,15). The square pyramidal complexes of Fe(II) and Co(II), which have good activity for  $O_2$  reduction, appear to involve such an end-on interaction (16). This adsorption of  $O_2$  is expected to be accompanied by at least a partial charge transfer to yield a superoxide and then peroxide state, as represented by Pathway II in Fig. 3. The adsorption of the  $O_2$  on the square pyramidal complexes of Fe(II) and Co(II) may lead directly to the superoxide state. With somewhat similar oxyhemoglobin complexes of iron, various workers have proposed that  $O_2$  binding to the iron involves  $O_2^-$  or  $O_2^{\cdot-}$  states with Fe in the III valent state (17,18). The change in valency state of the transition metal coupled with the change in  $O_2$  oxidation state during formation of the  $O_2$  adduct corresponds in principle to the redox electrocatalyst concept proposed by Beck *et al.* (19,20).

The further reduction of the  $O_2$  beyond the peroxide state requires rupture of the O-O bond. Such can occur in Pathway IIB through the formation of  $O^-$  or  $HO\cdot$  free radicals in solution or the simultaneous reduction-bond cleavage (electrochemical desorption) to

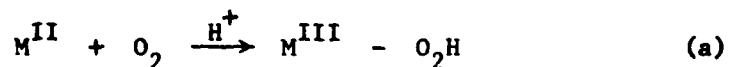
yield  $\text{H}_2\text{O}$  or  $\text{OH}^-$ . Neither of these processes is likely to be sufficiently fast at practical operating potentials for  $\text{O}_2$  cathodes but the electrochemical desorption is a better candidate. The free energies of formation of the  $\text{O}^-$  and  $\text{OH}^\cdot$  free radicals in solution are just too high to achieve sufficient concentrations of these species for the subsequent homogeneous reactions to proceed at rates corresponding to reasonable current densities at acceptable electrode potentials.

Pathway III in Fig. 3 provides an alternate means for bringing about rupture of the O-O bond through the formation of an -O-O-bridge. Such a mechanism may come into play with the proper spacing of transition metal elements in a binetal complex such as a macrocycle. The formation of the bridge species also requires that the two metal species have partially filled d-orbitals to participate in bonding with the  $\pi^*$  orbitals of the oxygen. Macrocyclic transition metal complexes of the type  $\text{M-O}_2\text{-M}$  have been synthesized (e.g., ref. 21-23) and appear to occur naturally in heme-thrin. Various solution phase macrocyclics including the tetrasulfonated phthalocyanines (M-TSP) have been reported to form  $\text{O}_2$  complexes of the type  $\text{M-TSP-O}_2\text{-M-TSP}$  (26-32) where M is Co or Fe.

For any of the mechanisms in Fig. 2 considerable questions exist as to the reversibility of the  $\text{O}_2$  adsorption step at the rather high rates involved with practical  $\text{O}_2$  cathodes. For  $\text{O}_2$  to bond to  $\text{M}^z$  will generally require the replacement of a water molecule or anion of the electrolyte -- a situation which would normally be expected to be unfavorable to  $\text{O}_2$  unless the  $\text{O}_2$  adduct has a pronounced dipolar character ( $\text{M}^{z+1}\text{O-O}^-$ ) (24,25).

### III. PRIOR STUDIES OF $\text{O}_2$ REDUCTION ON TRANSITION METAL MACROCYCLIC COMPLEXES

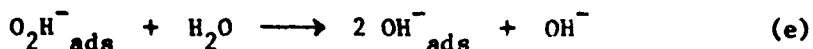
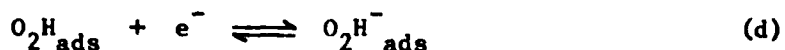
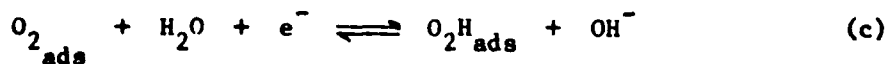
Metal phthalocyanines have been found to have catalytic activity for the heterogeneous  $\text{O}_2$  reduction (1,2,20,33-39). A direct correlation has been found (20,34,35) between the first oxidation potential of the metal phthalocyanine and catalytic activity for  $\text{O}_2$  reduction. Beck (20) has proposed a mechanism based on data for  $\text{O}_2$  reduction on Co tetraazaannulene (Co-TAA) which gives Tafel slopes of -60 mV/decade in acid solution. This author proposed that the metal complex reacts with oxygen according to the reaction:



where  $\text{O}_2$  undergoes partial reduction with simultaneous oxidation of the metal center. The  $\text{O}_2$  adduct, according to Beck, then undergoes a 2-electron reduction as the rate determining step, regenerating the catalyst. For a transfer coefficient  $\alpha = 0.5$ , the Tafel slope could then be -60 mV/decade. Simultaneous 2-electron steps, however, are

unlikely on energetic grounds.

On the basis of O<sub>2</sub> reduction data on Fe phthalocyanines, Appleby and Savy (36,39) propose that the rate-determining step is the breaking of the O-O bond with the mechanism:



#### IV. EXPERIMENTAL PROCEDURES

The present work has involved water soluble tetrasulfonated phthalocyanine adsorbed on graphite substrates (2,40). The redox properties of the catalysts have been examined using cyclic voltammetry. This approach has been facilitated by use of the basal plane of stress-annealed pyrolytic graphite (SAPG) with x-ray diffraction rocking angles as small as  $\Delta\theta_{1/2} = 0.4^\circ$ . This material has low background current (41) and very little activity for the O<sub>2</sub> reduction process (42). The O<sub>2</sub> reduction studies have been carried out with the rotating disk-ring electrode technique.

A disk electrode exposing the basal plane of SAPG (2) with an area of 0.20 cm<sup>2</sup> was used for the rotating disk measurements. For the ring-disk measurements, the disk was constructed with ordinary pyrolytic graphite (OPG) ( $\Delta\theta_{1/2} = 45^\circ$ , radius = 0.250 cm) with Au (99.99% pure) as the ring (inner radius = 0.272 cm, outer radius = 0.357 cm). The fragile nature of the SAPG prevented its use as the disk in the ring-disk experiments. Unless otherwise indicated, all measurements on SAPG and OPG were on the basal planes.

The Teflon cell had separate compartments for the reference (saturated calomel-SCE) and counter electrode (Au-foil) with an addition isolation compartment between the working and reference compartments. A Teflon Luggin capillary was used to minimize IR drop. All measurements were made at 20 to 22°C.

The surface of the basal plane of SAPG was renewed by use of the adhesive tape technique with care to avoid contamination of the Teflon mounting with the adhesive of the tape (2,42). The OPG electrodes were polished using 0.3μ alumina. The M-TSP was adsorbed on the graphite surface by placing a drop of solution of the complex (10<sup>-5</sup>M) on the electrode. The electrode was subsequently washed with

purified water. For experiments in acid solution some of the complex was added to the electrolyte to preserve the adsorbed catalyst layer during the measurements. In the other solutions the adsorption was sufficiently strong to render the loss of the adsorbed complex negligible over the duration of the measurements.

Basic (0.1M NaOH) and acid (0.05M H<sub>2</sub>SO<sub>4</sub>) solutions were prepared as described before (2). Solutions of pH were as follows: 1M NaOH: pH = 13.8; 0.1M NaOH: pH = 12.9; 0.1M Na<sub>2</sub>CO<sub>3</sub>: pH = -1.5; 0.005M Na<sub>2</sub>CO<sub>3</sub> + 0.05M Na<sub>2</sub>SO<sub>4</sub>: pH = 10.8; 0.0015M NaOH + 0.05M H<sub>3</sub>BO<sub>3</sub> + 0.05M Na<sub>2</sub>SO<sub>4</sub>: pH = 8.7; 0.10M NaOH + 0.05M H<sub>3</sub>BO<sub>3</sub> + 0.05M Na<sub>2</sub>SO<sub>4</sub>: pH = 6.3 and 0.1M NaH<sub>2</sub>PO<sub>4</sub>: pH = 4.4. Special precautions were taken to minimize CO<sub>3</sub><sup>2-</sup> in the alkaline electrolytes. The Co-TSP and Fe-TSP were prepared and purified by the procedures described by Weber and Busch (43).

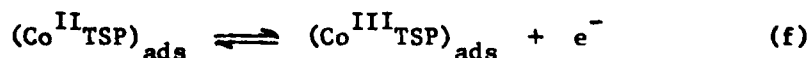
## V. RESULTS

### A. Voltammetry of Adsorbed Co-TSP and Fe-TSP

Figure 4 shows the voltammetry curves obtained at different potential scan rates for Co-TSP pre-adsorbed on the basal plane of SAPC. A Teflon hood (44) was used to eliminate edge effects and leakage of the electrolyte between the Teflon and the side of the disk electrode, which otherwise cause a pronounced slant to the voltammetry curves. The charge under the peak is 3 μC/cm<sup>2</sup>, which corresponds to a surface concentration of 3 x 10<sup>-11</sup> moles/cm<sup>2</sup> of adsorbed metal complex assuming a one-electron process. Assuming that the surface redox couple obeys the Nernst equation, the peak current is given by

$$i_p = \frac{n^2 F \Gamma v}{4 RT} \quad (1)$$

where  $\Gamma$  is the surface concentration,  $v$  is the potential scan rate and  $n$  is the number of electrons per adsorbed molecule. The charge under the peak is equal to  $Q = nF\Gamma$ . Experimental values of  $i_p$  and  $Q$  give  $n = 0.9$ , indicating that one electron is involved in the surface redox process, which is likely (45,46), i.e.,



For Co-TSP adsorbed on OPG, the charge from cyclic voltammetry is ~ 13 μC/cm<sup>2</sup> or ~ 4 times that of SAPG.

The Fe-TSP also readily adsorbed on SAPG as evidenced by the voltammetry curve (Fig. 5). From the scan rate dependence of both peaks I and II, a one-electron transfer is involved in each case. The charge under each peak estimated from the area between the solid

and dotted lines is  $\sim 3.0 \mu\text{C}/\text{cm}^2$  for SAPG and  $\sim 13 \mu\text{C}/\text{cm}^2$  for OPG, which are the same as for Co-TSP. (The charge is independent of  $v$  over the range 50 to 1000 mV/s.) This suggests that the surface coverages by Co-TSP and Fe-TSP species are essentially the same.

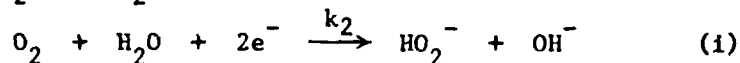
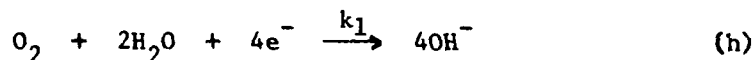
Peak I exhibits a pH dependence of 0.057 V/pH over the pH range 4.5 to 13 (Fig. 6). This peak is believed to involve the Fe(III)-TSP/Fe(II)-TSP couple. The pH dependence probably results from hydrolysis of the Fe(III) state (47,48). The redox reaction can then be written as



The position of peak II shifts with pH only at low pH values. It is not sure what process is involved for this reversible peak. Perhaps in the reduced form the electron is delocalized in the  $\pi$  system of the macrocyclic ligand or alternatively the Fe is in the equivalent of the I state. Lever and Wilshire (49) have reported that iron(II) phthalocyanine can be electrochemically reduced in non-aqueous solvents to give Fe(I)-Pc.

#### B. O<sub>2</sub> Reduction on Adsorbed Co-TSP

The rotating ring-disk data for O<sub>2</sub> reduction on Co-TSP/OPG in 0.1M NaOH are shown in Fig. 7. Using these data and the analysis of Wroblowa *et al.* (50), the O<sub>2</sub> reduction has been found to proceed through parallel processes with the reduction to the peroxide predominant and the overall 4-electron reduction minor (51). The usual rotating disk plots of  $i/i_L$  vs.  $1/\sqrt{\omega}$  also yield slopes,  $B$ , very close to those expected for a process yielding 2 electrons per O<sub>2</sub> diffusing through the boundary layer ( $B = 1.40 \times 10^2 \text{ mA}(\text{rpm})^{-1/2}$  as compared with a theoretical value (54) of  $1.42 \times 10^2 \text{ mA}(\text{rpm})^{-1/2}$  in 0.1M NaOH.) Fig. 8 indicates rate constants evaluated from the rotating disk-ring data for the two parallel processes:



The corresponding Tafel slopes are  $(\partial \ln k_1 / \partial E) = -0.15 \text{ V/decade}$  and  $(\partial \ln k_2 / \partial E) = -0.12 \text{ V/decade}$ . These slopes suggest that the first electron transfer is rate controlling for each pathway.

#### C. O<sub>2</sub> Reduction on Adsorbed Fe-TSP

Rotating ring-disk electrode data for Fe-TSP adsorbed on OPG are shown in Fig. 9 for 0.1M NaOH. The ring current was measured at the diffusion limiting HO<sub>2</sub><sup>-</sup> oxidation condition. The ring currents for disk potentials more positive than -0.32 V are zero, which indicates that the O<sub>2</sub> reduction occurs via 4 electrons with

no detectable peroxide at those potentials. The small amount of  $\text{HO}_2^-$  detected at higher polarizations may be due in part to  $\text{O}_2$  reduction on zones of the graphite not covered by Fe-TSP. The maximum in the disk current for the OPG substrate occurs almost at the same potential as for the Fe-TSP/OPG. The maximum in the disk current for the latter, however, is far too pronounced to be caused just by a substrate background current. This maximum for Fe-TSP/OPG correlates well with peak I in the voltammetry curve (Fig. 5). The analysis of the ring-disk currents at potentials cathodic to  $-0.45$  V indicates a large potential dependence for the ratio of disk-to-ring current at infinite rotation rate and hence parallel mechanisms appear operative.

Tafel plots for  $\text{O}_2$  reduction on Fe-TSP/OPG in solutions of various pH are shown in Fig. 10. The diffusion limiting current densities for the 4-electron  $\text{O}_2$  reduction are tabulated in the figure. The currents are first order in  $\text{O}_2$  concentration over the entire potential range. The lower linear Tafel region is pH dependent with slopes  $\sim -35$  mV/decade at pH 10.8 - 13.9 and increasing to  $-65$  mV/decade at pH 4.4. Reproducible data could not be obtained at pH below 4 because the adsorbed Fe-TSP decomposed when the potential was scanned to more cathodic potentials in acid electrolytes. This decomposition is accelerated by the presence of  $\text{O}_2$  and is probably caused by  $\text{HO}_2^-$  formation. Reaction order studies with respect to  $\text{OH}^-$  indicated that the reaction is inverse first order in  $\text{OH}^-$  at pH 10 to 3.8 and approaches zero order at lower pH (see Fig. 11). This correlates with the increase in Tafel slope at lower pH in Fig. 10.

The apparent limiting current at  $I/(I_L - I)$  values of  $\sim 0.8$  is particularly interesting. This current is not diffusion controlled and is first order in  $\text{O}_2$  concentration but independent of pH over the entire range studies. It is associated with the pre-wave in Fig. 9. A chemical limiting process with potential insensitive kinetics is involved.

Only rotating disk experiments were carried out on Fe-TSP adsorbed on SAPG (Fig. 12), but the behavior is similar to that on Fe-TSP/OPG. The  $1/i$  vs.  $1/\sqrt{\omega}$  plots indicate that at potentials anodic to  $-0.5$  V,  $\text{O}_2$  reduction proceeds virtually entirely by the overall 4-electron process without the generation of peroxide. At more cathodic potentials, these plots indicate substantial peroxide generation. This is not peroxide generation on bare portions of the SAPG surface since  $\text{O}_2$  reduction to either peroxide or  $\text{OH}^-$  is grossly inhibited on the basal plane in the absence of the adsorbed complexes (42).

The current-potential data can be deconvoluted into two component processes as shown in Fig. 13. The process corresponding to  $i_b$  has been assumed to follow Tafel linearity only at more cathodic potentials and to approach zero current at potentials negative to the

reversible value for the overall 4-electron reduction in order to fit the experimental data. Such behavior may occur if process b corresponds to a hydrogen peroxide producing reaction with the bulk peroxide concentration finite but low (e.g.,  $10^{-7}$  M). Small residual currents were observed on the ring after several cathodic potential sweeps, providing evidence for such peroxide. The curve corresponding to  $i_b$  then approaches the reversible potential for the  $O_2/HO_2^-$ ,  $OH^-$  couple for whatever is the bulk concentration of  $HO_2^-$ .

#### D. Specular Reflectance Studies of Adsorbed Co-TSP and Fe-TSP

Specular reflectance measurements have been carried out for Co-TSP and Fe-TSP adsorbed on the basal plane of SAPG, Au and Pt. The apparatus and techniques will be described in a separate publication (53). The Pt and Au surfaces were optically polished with  $Al_2O_3$  while fresh SAPG surfaces were prepared with the adhesive tape technique. The reflectance changes were recorded from 420 to 700 nm at  $45^\circ$  angle of incidence with both perpendicular and parallel polarization.

The reflectance spectra for Co-TSP on Pt are shown in Fig. 14 for both acid and alkaline electrolytes with and without  $O_2$  present. Figure 14 presents comparable data for Fe-TSP adsorbed on SAPG and Pt in 0.1M NaOH. These spectra are believed to represent the first time that the  $O_2$  adducts of Fe-TSP and Co-TSP adsorbed on surfaces have been observed. The transmission absorption spectra for the Co-TSP and Fe-TSP in  $O_2$  saturated alkaline and acid solutions, measured in the present study (53), also indicate the formation of  $O_2$  adducts in solution, including the adduct M-TSP- $O_2$ -M-TSP. The spectral changes associated with the formation of the  $O_2$  adduct with the adsorbed Co-TSP and Fe-TSP are similar to those occurring with the formation of the corresponding  $O_2$  solution phase adducts in acid and alkaline solutions.

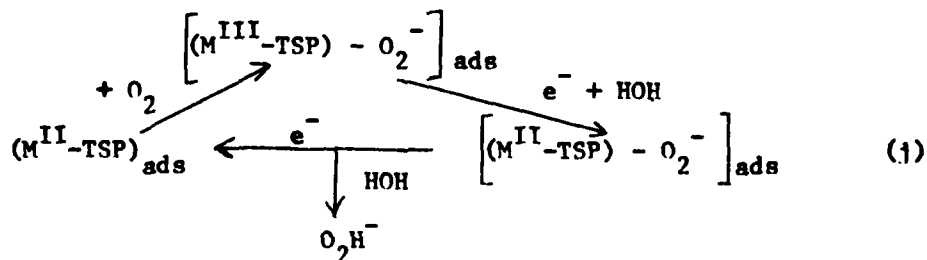
The configuration of the adsorbed complex relative to the surface is not fully clear. The most likely configuration is with the macrocyclic structure parallel to the surface and with the transition metal interacting with the surface through an -O- linkage. Such a configuration would not easily provide for -O-O- bridging between transition metal sites with two adjacent complexes or between one metal site and the carbon surface. It is unlikely that the M-TSP complexes are adsorbed on the electrode surfaces with the macrocyclic ligand parallel and immediately adjacent to the surface (i.e., in the inner Helmholtz plane). The peaks in the 600-680 nm range for the adsorbed species occur at nearly the same wavelengths as for the bulk solution species. On the other hand, the  $\pi-\pi^*$

parallel transition is sensitive to the immediate dielectric environment adjacent to the macrocyclic ligand and would be perturbed by the interaction with the graphite  $\pi$  orbitals or metal orbitals if in direct contact with the surface. An alternative possibility is that these macrocyclic complexes are edge-on adsorbed with the sulfonate groups interacting with the surfaces. This arrangement would facilitate -O-O- bridging.

Further UV-visible reflectance studies using polarized light and Raman studies are planned to gain more information concerning how these species are adsorbed.

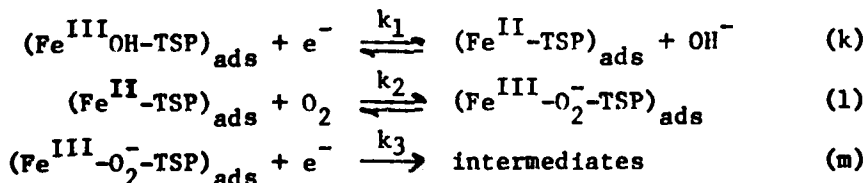
#### VI. MECHANISTIC CONSIDERATIONS OF $O_2$ REDUCTION ON ADSORBED Co-TSP and Fe-TSP

The  $O_2$  reduction to peroxide on Co-TSP/graphite may proceed according to the following scheme:



where the first step is probably ligand displacement (water or  $OH^-$  groups, depending on pH), followed by a heterogeneous electron transfer to yield the peroxide with this step rate controlling.

The more cathodic peak in the voltammetry curves for Fe-TSP (Peak II in Fig. 5) occurs at potentials in the lower polarization region (Fig. 10) where deviations from Tafel linearly become evident. This suggests an involvement of the  $(Fe^{III}OH\text{-TSP})_{\text{ads}}/(Fe^{II}\text{-TSP})_{\text{ads}}$  couple in the reaction mechanism responsible for current component  $i_a$ . The following mechanism explains the behavior of this component for  $pH > 8$ :



with reaction m normally rate controlling. On the basis of the kinetic evidence, the pathway appears to involve only one adsorbed M-TSP complex at a time, and therefore, not a bridge between the transition metal centers in two complexes. The possibility exists for -O-O-

bridging between the surface and the transition metal but this seems unlikely.

In the lower Tafel linear region, reaction m is rate controlling while the limiting current  $(i_a)_L$  is associated with reaction 1 becoming controlling. The corresponding kinetic equation is (50,51)

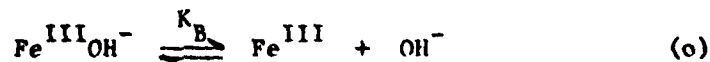
$$i_a = (i_a)_L \frac{(\text{OH}^-)^{-1} K \exp \left[ -(1+\alpha) \frac{F}{RT} (E-E_0) \right]}{\left[ 1 + (\text{OH}^-)^{-1} \exp \left[ -\frac{F}{RT} (E-E_0) \right] \right] \left[ 1 + K \exp \left[ -\frac{\alpha F}{RT} (E-E_0) \right] \right]} \quad (2)$$

$$\text{where } (i_a)_L = 4 F k_2 (\text{O}_2)_m \quad (3)$$

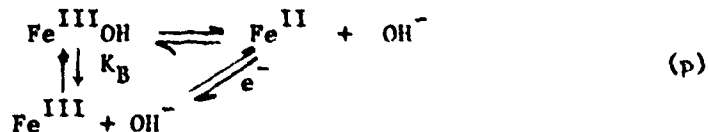
with  $m$  the surface concentration of Fe-TSP,  $E_0$  the standard electrode potential for reaction m,  $\alpha$  the transfer coefficient for this step,  $K = k_3/k_{-2}$ , and  $(\text{OH}^-)$  and  $(\text{O}_2)$  the  $\text{OH}^-$  and  $\text{O}_2$  concentrations.

This equation predicts the essential features of the experimental data below the high polarization-Tafel linear region in the pH range from 8.7 to 13.8; i.e. the reaction rate is first order in  $(\text{O}_2)$  and  $-1$  in  $(\text{OH}^-)$ , and predicts a limiting current density  $(i_a)_L$  which is directly proportional to  $\text{O}_2$  concentration, to Fe-TSP surface concentration and independent of pH. The quantity  $(i_a)_L$  is due to a potential insensitive chemical process, reaction 1, which becomes rate controlling when the Fe(II)-TSP species approach saturation and the cathodic polarization has increased the rate of reaction m to a relatively high value. According to this proposed mechanism, the Tafel slope for the linear Tafel region of  $i_a$  should be  $-RT/((1+\alpha)F)$ . The value of the slope will depend on the value of  $\alpha$ . For  $\alpha = 0.5$  the slope is  $-RT/(1.5F)$  or  $-40$  mV/decade and for  $\alpha = 1$  is  $-RT/(2F)$ , or  $-30$  mV/decade, as compared with an experimental value of  $\sim -35$  mV/decade.

At more acidic pH it is necessary to consider the acid-base equilibrium:



The redox process may be represented as



with the TSP ligand not shown. The mechanism can then be modified for low pH ( $< 8$ ) by replacing reaction k by reaction p followed with

reaction 1 as rate controlling. The current component  $i_a$  is then

$$i_a = 4Fk_2(\text{Fe}^{\text{II}})(\text{O}_2) \quad (4)$$

and, taking into account reaction p and considering low pH (< 4), becomes

$$i_a = (i_a)_L \frac{K_B^{-1} \exp\left(-\frac{F}{RT}(E-E_o)\right)}{1 + K_B^{-1} \exp\left(-\frac{F}{RT}(E-E_o)\right)} \quad (5)$$

This equation fits the experimental observation that at low pH  $i_a$  has relatively little or no pH dependence (see Fig. 11). These two mechanisms are expected to be competitive in the pH range between 10 and 4. This would explain the gradual change in the Tafel slope from -30 mV/decade to -60 mV/decade.

At high cathodic polarization, the  $\text{O}_2$  reduction mechanism probably reverts to a pathway similar to that proposed for the Co-TSP/graphite system (reaction j).

#### VII. IMPLICATIONS OF RESEARCH

Some transition metal macrocyclics such as the adsorbed Fe-TSP are active catalysts for the overall 4-electron reduction of  $\text{O}_2$ . The kinetics, however, are reasonably well explained by pathways which do not involve bridged -O-O- adducts and are first order rather than second order with respect to the surface concentrations of Fe-TSP. The reflectance spectra indicate the formation of  $\text{O}_2$  adducts with the adsorbed Co-TSP and Fe-TSP but these spectra also do not provide any specific evidence for bridged -O-O- adducts.

The most critical feature of the 4-electron reduction appears to be the location of the potential for the Fe(II)-TSP/Fe(III)-TSP couple at a value near that at which the  $\text{O}_2$  reduction occurs. The pH dependence of this potential, however, is such that the catalytic activity for the 4-electron reduction is depressed with increasing  $\text{OH}^-$  ion concentration. On the other hand, the 2-electron reduction to the peroxide is essentially independent of  $\text{OH}^-$  activity. As a consequence, in the concentrated bases used in most fuel cell and air battery applications, the peroxide generation becomes significant even at low current densities and this in turn leads to accelerated attack of the Fe-TSP as well as the graphite or carbon surfaces.

ACKNOWLEDGMENT: This research has been supported by the Office of Naval Research (optical studies) and the Department of Energy through a subcontract from the Diamond Shamrock Corporation ( $\text{O}_2$  re-

duction studies). One of the authors (JZ) has held a fellowship from the Organization of American States during part of this work, while a second (BZN) held a postdoctoral fellowship from the Research Fund of the Socialistic Republic of Serbia, Yugoslavia during part of this work.

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  54. See eq. 2 in ref. 2 and the discussion therein.



Figure 1. Interaction of  $\pi$  and  $\pi^*$  molecular orbitals of  $O_2$  with  $d$  orbitals of a metal in Griffiths model.

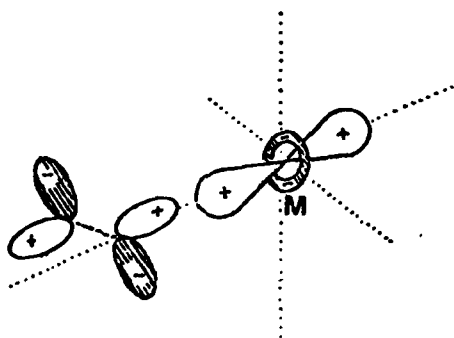


Figure 2. Interaction of  $\pi^*$  molecular orbital of  $O_2$  with  $d_{z^2}$  orbital of a metal in Pauling model.

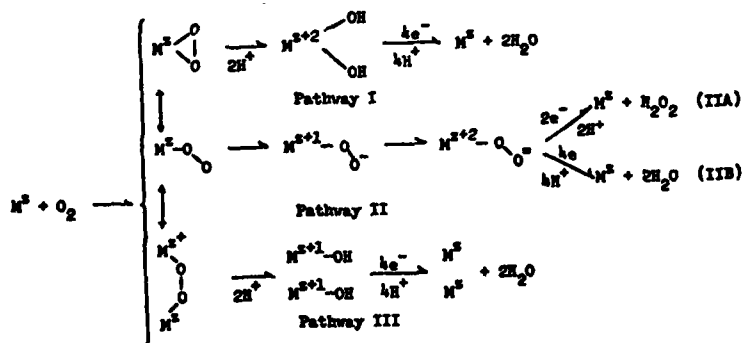


Figure 3. Reaction pathways for  $O_2$  electroreduction in acid electrolytes (Yeager (12)).

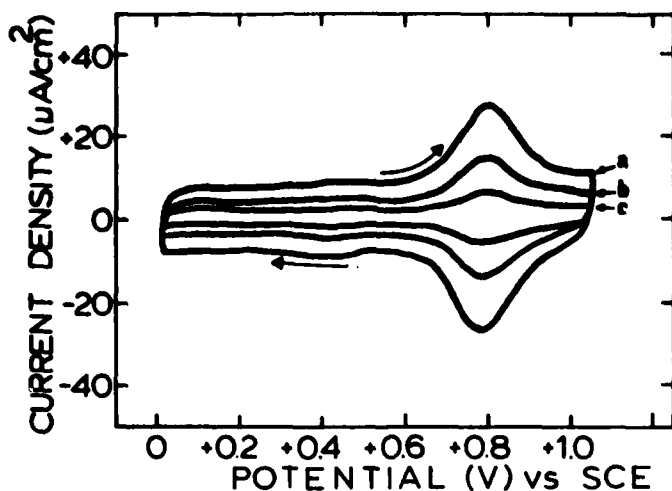


Figure 4. Cyclic voltammograms at different scan rates for Co-TSP adsorbed on SAPG. Electrolyte: 0.05M  $H_2SO_4$ . (No Co-TSP in solution; obtained with hood to block electrolyte at edge of disk).

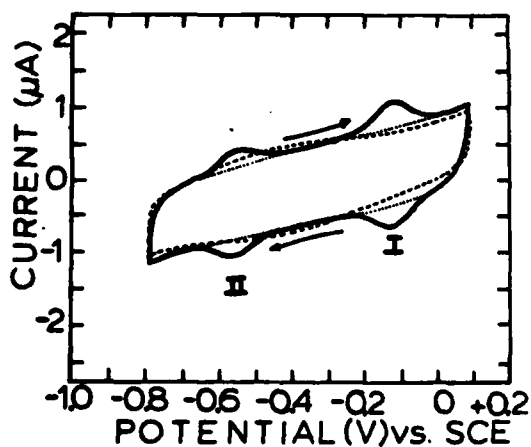


Figure 5. Cyclic voltammogram with (solid line) and without (dashed line) Fe-TSP pre-adsorbed on SAPG. Supporting electrolyte: 0.1M NaOH, He saturated. Scan rate: 500 mV/s (obtained without hood).

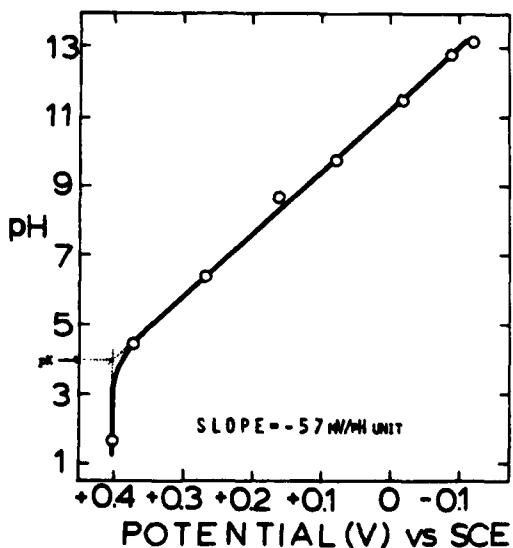


Figure 6. pH dependence of the potential of peak I in the voltammetry (see Fig. 5) for Fe-TSP adsorbed on OPG.

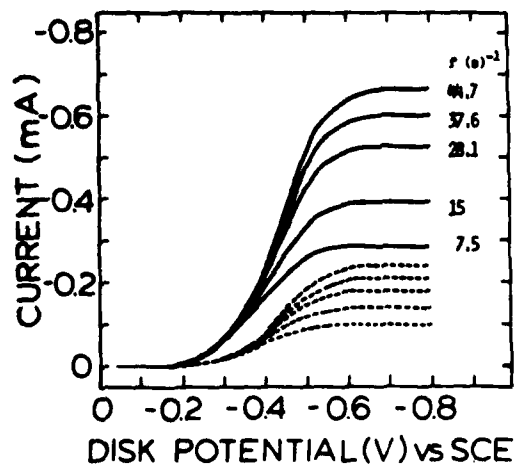


Figure 7. Rotating ring-disk data for  $O_2$  reduction on Co-TSP pre-adsorbed on OPG in 0.1M NaOH. Disk current indicated by solid lines; ring current by dashed lines. Scan rate: 10m V/s. Ring potential: +0.1V vs SCE. Ring currents are anodic. Collection efficiency:  $N = 0.38$ .

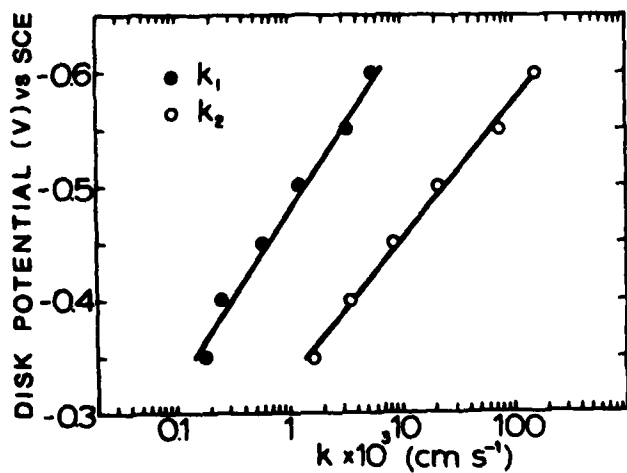


Figure 8. Potential dependence of the heterogeneous rate constants for the  $4e^-$  reduction ( $k_1$ ) and  $2e^-$  reduction ( $k_2$ ) of  $O_2$  on Co-TSP adsorbed on OPG in 0.1M NaOH.

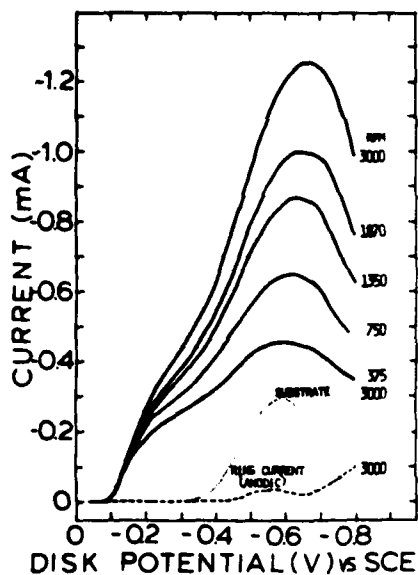


Figure 9. Rotating ring-disk data for  $O_2$  reduction on Fe-TSP pre-adsorbed on the disk of OPG. Disk currents in solid lines; ring currents in dashed lines; current on OPG disk without Fe-TSP, dotted line. Electrolyte: 0.1M NaOH. Scan rate: 5m V/s. Ring potential: +0.1V vs SCE. Collection efficiency:  $N=0.38$ .

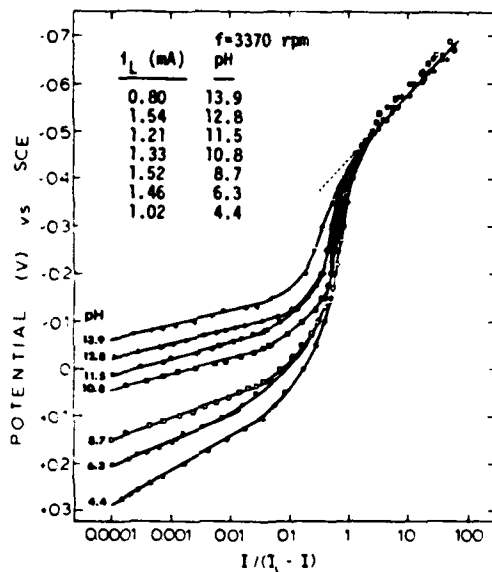


Figure 10. Tafel plots for  $O_2$  reduction on Fe-TSP adsorbed on OPG in solution of various pH values. Rotation Rate: 3370 rpm

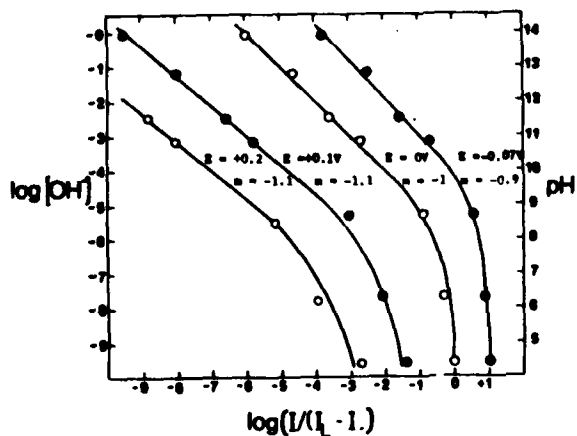


Figure 11. Plots of  $\log(I/(I_L - I))$  vs  $\log(OH^-)$  for values of  $I/(I_L - I)$  taken from the Tafel linear region of low polarization in Fig. 10 extrapolated, if necessary, at a constant potential.

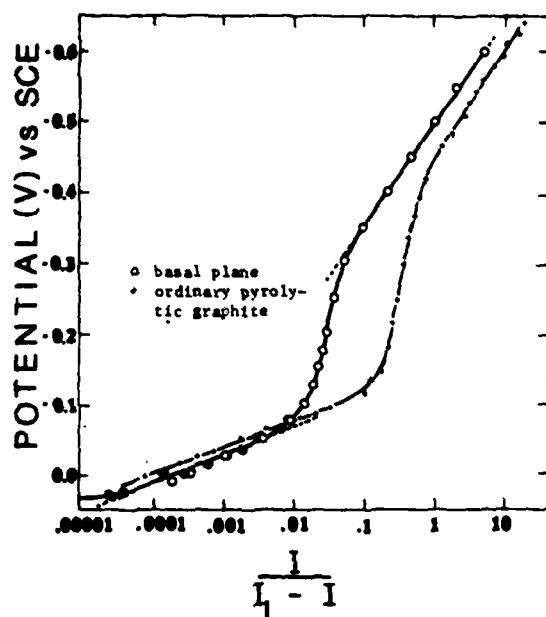


Figure 12. Tafel plot of  $\log(I/(I_L - I))$  vs  $E$  for  $O_2$  reduction on Fe-TSP adsorbed on SAPG and OPG at  $F=3000$  rpm in  $0.1M$  NaOH.

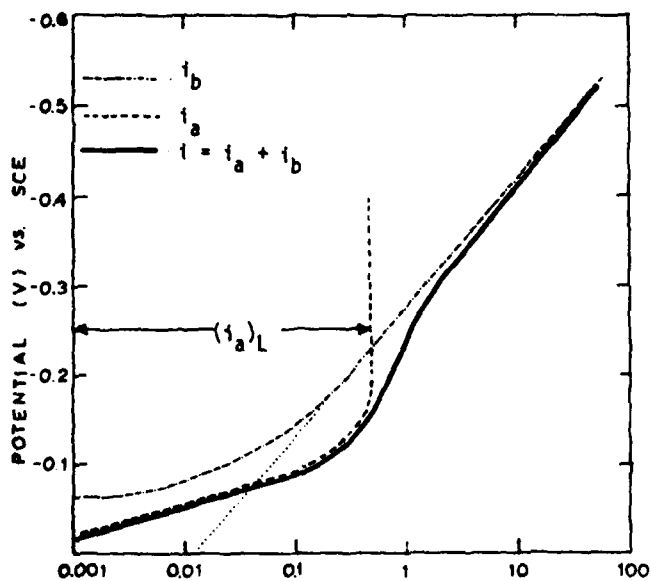


Figure 13. Graphical representation of the combination of two processes for  $O_2$  reduction on adsorbed Fe-TSP in basic media.

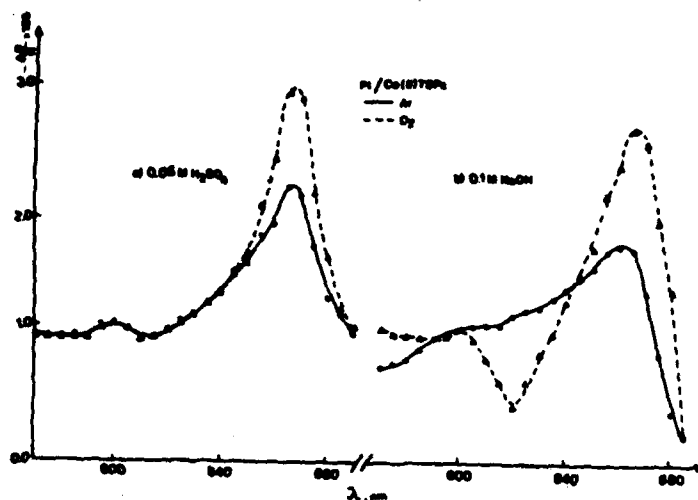


Figure 14. Reflectance spectra of Co(II)-TSP adsorbed on Pt at 0.70V vs RHE in 0.05M  $H_2SO_4$  (a) and 0.1M NaOH (b) with argon and  $O_2$  saturated solutions. Parallel optical polarization.

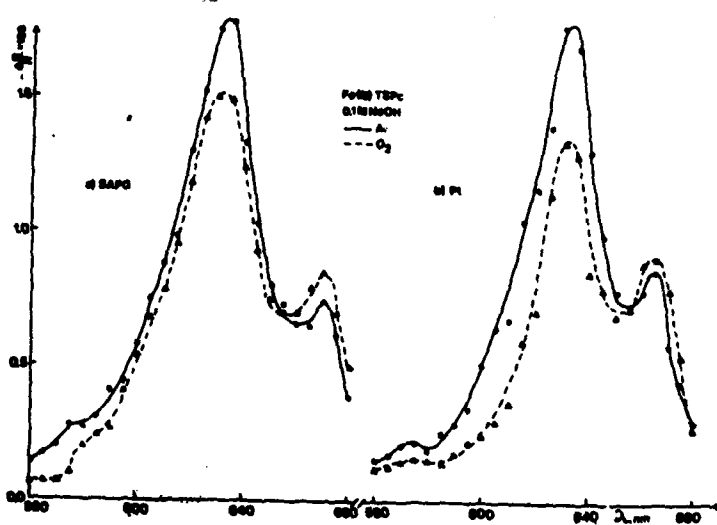


Figure 15. Reflectance spectra of Fe(III)-TSP adsorbed on basal plane of SAPG at 0.90V vs RHE (a) and on Pt at 0.70V vs RHE (b) with argon and  $O_2$  saturated solutions. Perpendicular optical polarization.

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