J. Am. Chem. Soc. **1983**, *105*, 2950–2955

mol^{-1} for the bifluoride ion is quite reliable..

It is of interest in this connection to examine the enthalpy change for the formation of the assymmetrical proton-bound dimer, FH_2O^-, given by eq 21. In previous work, we concluded

$$FHF^- + HOH_2O^- \rightarrow 2FH_2O^- \qquad (21)$$

that the enthalpy change for this type of reaction is close to zero for strong-hydrogen-bonded systems and approximately equal to the enthalpy in transfering a proton from the strong acid to the anion of the weaker acid (−10.3 kcal in this case) for a weak-hydrogen-bonded system. From a simple thermochemical cycle, we calculate a value of $\Delta H_{21}° = -1.9$ kcal, close to what we would expect from our previous conclusion that the R–O–H–F$^-$ system was a strong-H-bonded one. Alternatively by setting $\Delta H_{21}° = 0$, one can calculate an expected upper limit to the value of $D(F^-{-}HF)$ of 40.9 kcal from previously measured dissociation energies of $F{-}H_2O^-$ and $OH(H_2O)^-$.[20] This estimate is in good agreement with our directly measured value.

As demonstrated by the data in Figure 3, the fluoride affinities of HF and HCN are very nearly equal. However, the lower energy dissociation pathway for $FHCN^-$ (eq 22) gives rise to a hydrogen-bond energy in $FHCN^-$ of only 21 kcal mol^{-1}. The chemical stability of this adduct has recently been demonstrated by Ault[58] who has succeeded in synthesizing and characterizing $FHCN^-$ in low-temperature matrices. In contrast to results reported previously by Sullivan and Beauchamp,[59] we do not see the HF displacement reaction (eq 23) producing the bicyanide ion. In their study, $FHCN^-$ had been generated by fluoride transfer from FSO_2^- (eq 24) formed from dissociative electron attachment to SO_2FCl. However, the data of Table I reveal that this reaction is endothermic by 4 kcal mol^{-1}, implying that the FSO_2^- formed from SO_2FCl has some internal excitation that is transferred to some extent to $FHCN^-$ subsequently permitting eq 23 to occur. The extreme slowness of eq 23 observed by Sullivan and Beauchamp is further evidence that this process may be an endothermic reaction. Our results thus indicate that $D(CN^-{-}HCN)$ is less than $D(CN^-{-}HF)$, although the difference is probably small.

$$FHCN^- \rightarrow CN^- + HF \qquad (22)$$

$$FHCN^- + HCN \nrightarrow H(CN)_2^- + HF \qquad (23)$$

$$FSO_2^- + HCN \rightarrow FHCN^- + SO_2 \qquad (24)$$

Conclusion

The results presented here demonstrate that a quantitative fluoride affinity scale for Brønsted acids has been established. The ordering of fluoride affinities of various functional groups provides a rational basis for understanding the ability of these groups to solvate anions. The data also provide some basis for understanding the differences in gas-phase and solution acidity behavior that are frequently observed. Within a homologous series of acids, it has been demonstrated that a correlation of gas-phase acidity and fluoride affinity exists. For different functional group types, however, such a correlation completely breaks down. For different acid types, a dependence of fluoride binding energy on electronegatively of the heteroatom involved is implicated. Finally, and perhaps most significantly, the hydrogen-bond energy in the bifluoride ion has been determined to be 38.6 kcal mol^{-1}, in good agreement with selected experimental and theoretical studies.

Acknowledgment. Financial support of the National Sciences and Engineering Research Council Canada (NSERC) is gratefully acknowledged. We thank M. Roy for the synthesis of ketene and for calculations of moments of inertia and geometries of fluoride adducts.

Registry No. F^-, 16984-48-8; HCO_2H, 64-18-6; SO_2, 7446-09-5; CH_3CO_2H, 64-19-7; SF_4, 7783-60-0; COF_2, 353-50-4; PhOH, 108-95-2; HCN, 74-90-8; PF_3, 7783-55-3; HF, 7664-39-3; CF_3CH_2OH, 75-89-8; SOF_2, 7783-42-8; $(CH_2F)_2CHOH$, 453-13-4; H_2S, 7783-06-4; $(CHF_2)_2O$, 1691-17-4; SO_2F_2, 2699-79-8; CH_2CO, 463-51-4; CH_3SH, 74-93-1; CH_2FCH_2OH, 371-62-0; *t*-C_4H_9OH, 75-65-0; *n*-C_3H_7OH, 71-23-8; *i*-C_3H_7OH, 67-63-0; *n*-C_4H_9OH, 71-36-3; C_2H_5OH, 64-17-5; $PhNH_2$, 62-53-3; C_2F_5CN, 422-04-8; CH_3OH, 67-56-1; C_2F_5H, 354-33-6; $CF_3CH_2NH_2$, 753-90-2; CF_3H, 75-46-7; CF_2HCH_2F, 430-66-0; C_2F_3H, 359-11-5; H_2O, 7732-18-5; $(CH_3)_3CCHO$, 630-19-3; $PhCH_2F$, 25496-08-6; *t*-C_4H_9F, 353-61-7; 1-*H*-pyrrole, 109-97-7; (fluoromethyl)oxirane, 503-09-3.

---

[58] Ault, B. S. *Acc. Chem. Res.* **1982**, *15*, 103.

[59] Sullivan, S. A.; Beauchamp, J. L. *Int. J. Mass. Spectrom. Ion Phys.* **1978**, *28*, 69.

Reversible Oxidation and Rereduction of Entire Thin Films of Transition-Metal Phthalocyanines

J. Mark Green and Larry R. Faulkner*

Contribution from the Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801.

Received August 30, 1982

Abstract: Thin films (1000–2000 Å thick) of iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) phthalocyanines (Pc) on gold or indium oxide electrodes undergo stoichiometric oxidation and rereduction. Except for FePc and CoPc, the process is essentially reversible. Chronocoulometry showed that ZnPc films oxidized to the extent of 1.21 electrons per ZnPc molecule; CoPc required 1.92 electrons per molecule. Charge compensation is attained upon oxidation by uptake of anions from the electrolyte and by expulsion of anions upon reduction. Auger electron spectrometry allowed detection of the ions and characterization of their distributions. In partially oxidized films, the anions appear to be homogeneously distributed. Oxidation seems to proceed at all grains with equal probability, with anions entering and departing along grain boundaries. Smaller anions allow full oxidation at rapid rates; larger ones inhibit the oxidation with respect to rate. Optical spectroscopy showed evidence for reorganization of the crystalline lattices. The rereduced form is not the same as the original material, but it can be restored to the original form by annealing at 125 °C. In cyclic oxidations and rereductions, there is a gradual loss of charge-consuming ability, apparently related to electrical isolation of small domains, perhaps grains. The oxidations and rereductions are electrochromic, and the various color changes are described.

Phthalocyanines have received much attention recently in a wide range of contexts,[1] particularly as thin films. Their catalytic properties, principally in the electroreduction of O_2, have been studied extensively.[2–6] A large volume of related research has

0002-7863/83/1505-2950$01.50/0

dealt with their photochemical[8,9] and electrochemical[10–21] properties, as well as their behavior as semiconductors in solid-state devices[8,22–34] and as electrodes in electrochemical cells.[28,31,35,36] Phthalocyanine films have been used for spectral sensitization or protection of more conventional semiconductors[37–40] employed in photoelectrochemical cells.

The role of absorbed oxygen as an adventitious dopant leading to p-type semiconductivity in some crystalline forms of these materials is reasonably well understood.[25–31] More recently, work by Marks and co-workers[41–45] and by Orr and Dahlberg[46] has shown that carefully designed, partially oxidized phthalocyanine phases can show metallic conductivity. In this paper, we report a very general capacity of compact thin films of phthalocyanines, exposed to aqueous solutions of electrolytes, to undergo controllable degrees of oxidation and rereduction in a reversible manner. Stoichiometric uptake and expulsion of charge-compensating ions occurs during these processes and there is extensive reorganization of the crystalline lattice, but the films remain compact. Since the oxidized and reduced phases differ in color, the process gives rise to reversible electrochromism, which is interesting in itself. However, we want to point out that the phenomenon may be generally important in defining the species actually present on an electrode in electrochemical applications ranging from catalysis to spectral sensitization. It may even be useful for the synthesis of highly conducting, partially oxidized films of phthalocyanines.

Electrochromism in rare-earth diphthalocyanines has been recognized for some time and has been of interest for display applications. Lutetium diphthalocyanine, $Lu^{3+}H^{+}(Pc_2)^{4-}$, films have received the most study.[47–55] Nicholson and Pizzarello have studied $LuHPc_2$ films that were sublimed in vacuo onto either alumina, Mylar, or single-crystal sapphire.[48,51,52,54] Usually the lower end of a film was immersed in an electrolyte and the upper end was connected ohmically to an external circuit passing through a power supply to a counter electrode also immersed in the electrolyte. A constant anodic current was applied and a color change from green to red, starting at the dye–solution interface, propagated up the film. The loss of electrons during this oxidation was shown to be compensated by migration of anions into the film:

$$\underset{\text{green}}{LuHPc_2} + yA^{z-} \rightarrow \underset{\text{red}}{LuHPc_2{\cdot}yA} + ne \ (n = yz)$$

Values of n approximately equal to 2 were obtained for oxidations carried out with KCl and $NaSO_4$ solutions.[48] The influence of water vapor and oxygen on the rate of color change was also studied.[52] Ambient water vapor was required for the anodic process with both Cl^- and SO_4^{2-} electrolytes. Moreover, oxygen was required for oxidation in SO_4^{2-} electrolyte.

$LuHPc_2$ films were also vacuum sublimed onto a tin oxide coated glass substrate[50] and were totally immersed in the electrolyte solutions. The optical transmission of such films was monitored at 670 nm, along with potential transients under constant applied current. The results of the experiments were interpreted by a two-layer space–charge model for the oxidation of $LuHPc_2$, involving the idea that the oxidation proceeds in a front from the electrolyte interface, through the film, to the tin oxide interface.

Electrochromism has also been reported for yttrium, scandium, ytterbium, and erbium diphthalocyanine films.[47,53,56] Results similar to those for lutetium diphthalocyanine films were obtained.

To our knowledge, there has been only one report of electrochromism in films of single-ring metal phthalocyanine complexes outside our laboratory. Gavrilov et al. have described the electrochromism of tetra-4-*tert*-butyl derivatives of CoPc and ZnPc

---

(1) Sayer, P.; Gouterman, M.; Connell, C. R. *Acc. Chem. Res.* **1982**, *15*, 73.

(2) Jasinski, R. *Nature (London)* **1964**, *201*, 1212.

(3) Meier, H.; Albrecht, W.; Tschirwitz, V.; Zimmerhackl, E. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 843.

(4) Appleby, A. J.; Savy, M. In "Electrode Materials and Processes for Energy Conversion and Storage"; McIntyre, J. D. E., Srinivasan, S., Will, F. G., Eds.; The Electrochemical Society Softbound Proceeding Series: Princeton, NJ, 1977; p 321.

(5) Appleby, A. J.; Fleisch, J.; Savy, M. *J. Catal.* **1976**, *44*, 281.

(6) Zagal, J.; Sen, R. K.; Yeager, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *83*, 207.

(7) Maroie, S.; Savy, M.; Verbist, J. J. *Inorg. Chem.* **1979**, *18*, 2560.

(8) Langford, C. H.; Hollebone, B. R.; Vandermoot, T. *Adv. Chem. Ser.* **1980**, *184*, 139.

(9) Darwent, J. R.; McCubbin, I.; Phillips, D. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 347.

(10) Rollman, L. T.; Iwamoto, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 1455.

(11) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982.

(12) Lexa, D.; Reix, M. *J. Chim. Phys. Phys.-Chim. Biol.* **1974**, *71*, 511.

(13) Clack, D. W.; Woolsey, I. S.; Hush, N. S. *Inorg. Chim. Acta* **1976**, *19*, 129.

(14) Lever, A. B. P.; Wilshire, J. P. *Can J. Chem.* **1976**, *54*, 2514.

(15) Lever, A. B. P.; Wilshire, J. P. *Inorg. Chem.* **1978**, *17*, 1145.

(16) Lever, A. B. P.; Minor, P. C. *Inorg. Chem.* **1981**, *20*, 4015.

(17) Lever, A. B. P.; Minor, P. C.; Wilshire, J. P. *Inorg. Chem.* **1981**, *20*, 2550.

(18) Gavrilov, V. I.; Luk'yanets, E. A.; Shelepin, I. V. *Elektrokhimiya* **1981**, *17*, 1183.

(19) Lever, A. B. P.; Pickens, S. R.; Minor, P. C.; Licoccia, S.; Ramaswamy, B. S.; Magnell, K. *J. Am. Chem. Soc.* **1981**, *103*, 6800.

(20) Mezza, T. M.; Armstrong, N. R.; Ritter, G. W., II; Iafalice, J. P.; Kenney, M. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *137*, 227.

(21) Sheperd, V. R., Jr.; Armstrong, N. R. *J. Phys. Chem.* **1979**, *83*, 1268.

(22) Gutmann, F.; Lyons, L. E. "Organic Semiconductors"; Wiley: New York, 1968.

(23) Sussmann, A. *J. Appl. Phys.* **1967**, *38*, 2738.

(24) Harrison, S. E.; Ludewig, K. H. *J. Chem. Phys.* **1966**, *45*, 343.

(25) Sakai, Y.; Sadaska, Y.; Yokouchi, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1886.

(26) Ghosh, A. K.; Morel, D. L.; Feng, T.; Shaw, R. F.; Rowe, C. A., Jr. *J. Appl. Phys.* **1974**, *45*, 230.

(27) Tachikawa, H.; Faulkner, L. R. *J. Am. Chem. Soc.* **1978**, *100*, 4379.

(28) Fan, F. R.; Faulkner, L. R. *J. Chem. Phys.* **1978**, *69*, 3334.

(29) Fan, F. R.; Faulkner, L. R. *J. Chem. Phys.* **1978**, *69*, 3341.

(30) Hall, K. J.; Bonham, J. S.; Lyons, L. E. *Aust. J. Chem.* **1978**, *31*, 1661.

(31) Faulkner, L. R.; Tachikawa, H.; Fan, F. R.; Fischer, S. G. *Adv. Chem. Ser.* **1980**, *184*, 113.

(32) Popovic, Z. D.; Loutfy, R. O. *J. Appl. Phys.* **1981**, *52*, 6190.

(33) Twarowski, A. J. *J. Chem. Phys.* **1982**, *76*, 2640.

(34) Popovic, Z. D. *J. Chem. Phys.* **1982**, *76*, 2714.

(35) Fan, F. R.; Faulkner, L. R. *J. Am. Chem. Soc.* **1979**, *101*, 4779.

(36) Armstrong, N. R.; Shepard, V. R., Jr. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *131*, 113.

(37) Minami, N.; Watanabe, T.; Fujishima, A. J.; Honda, K. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 476.

(38) Jaeger, C. D.; Fan, F. R.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 2592.

(39) Giraudeau, A.; Fan, F. R.; Bard, A. J. *J. Am. Chem. Soc.* **1980**, *102*, 5137.

(40) Leempoel, P.; Castro-Acuna, M.; Fan, F. R.; Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 1396.

(41) Peterson, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286.

(42) Schramm, C. J.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Science (Washington, D.C.)* **1978**, *200*, 47.

(43) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1979.

(44) Marks, T. J.; Schoch, K. F., Jr.; Kundalkar, B. R. *Synth. Met.* **1979**, *1*, 337.

(45) Dirk, C. W.; Mintz, E. A.; Schoch, K. F., Jr.; Marks, T. J. *J. Macromol. Sci., Chem.* **1981**, *A16*, 275.

(46) Orr, W. A.; Dahlberg, S. C. *J. Am. Chem. Soc.* **1979**, *101*, 2875.

(47) Moskalev, P. N.; Kirin, I. S. *Russ. J. Phys. Chem. (Engl. Transl.)* **1972**, *46*, 1019.

(48) Nicholson, M. M.; Pizzarello, F. A. *J. Electrochem. Soc.* **1979**, *126*, 1490.

(49) Gavrilov, V. I.; Butasova, N. V.; Luk'yanets, E. A.; Shelepin, I. V. *Electrokhimiya* **1980**, *16*, 1611.

(50) Nicholson, M. M.; Pizzarello, F. A. *J. Electrochem. Soc.* **1980**, *127*, 821.

(51) Pizzarello, F. A.; Nicholson, M. M. *J. Electron. Mater.* **1980**, *9*, 231.

(52) Nicholson, M. M.; Pizzarello, F. A. *J. Electrochem. Soc.* **1980**, *127*, 2617.

(53) Walton, D.; Ely, B.; Elliott, G. *J. Electrochem. Soc.* **1981**, *128*, 2479.

(54) Nicholson, M. M.; Pizzarello, F. A. *J. Electrochem. Soc.* **1981**, *128*, 1288.

(55) Nicholson, M. M.; Pizzarello, F. A. *J. Electrochem. Soc.* **1981**, *128*, 1741.

(56) Yamana, M. *Oyo Butsuri* **1979**, *48*, 441.

that had been "rubbed" onto In_2O_3-coated glass.[49] Cyclic voltammetric experiments showed two oxidative peaks. The first peak (E_p = ~0.9 V vs. SCE) was quasi-reversible (ΔE_p = 80 mV) at a scan rate of 0.4 V/min. The second peak (E_p = 1.7 V vs. SCE) was irreversible. These results were interpreted as being the first and second one-electron ring oxidations of these phthalocyanine complexes. In the case of the CoPc derivative, a metal oxidation was also speculated to have taken place in the second oxidation process.

Our work was stimulated by the earlier research of Kahl in this laboratory, who seems to have been first to demonstrate reversible stoichiometric oxidation of a compact film of a simple phthalocyanine.[57] His efforts concerned MgPc. In this paper, we discuss the behavior of FePc, CoPc, NiPc, CuPc, and ZnPc films, with the focus principally on ZnPc. The mechanism by which the electrochromic reaction takes place in these single-ring phthalocyanine materials has been studied by a variety of methods. Cyclic voltammetric experiments show different results than those reported by Gavrilov et al. for derivatized CoPc and ZnPc materials.[49] Chronocoulometry has been used to determine *n* values for the oxidation of ZnPc and CoPc. During the oxidation of ZnPc films, anions from the electrolyte enter the films to maintain charge balance. The mechanism of entrance of anions into the films has been studied by Auger electron spectrometry.

Experimental Section

Phthalocyanine thin films (~1600 Å thick) were vapor deposited by using a Varian NRC 3117 vacuum bell jar system. Depositions were performed at approximately 5 × 10^{-6} torr and at rates of 1–10 Å/s. Films were deposited onto glass slides previously coated through a mask with 70 Å of Cr and then with 300 Å of Au. The glass slides had been cleaned initially by placing them in aqua regia for ~12 h, rinsing with distilled deionized water, and washing with hot isopropanol in a Soxhlet extractor. The pattern used for the Au and Cr layers was similar to that employed earlier by Fan.[35] The zone of gold underlying the part of the phthalocyanine layer in contact with solution was a disk 1.27 cm^2 in area. Films used for recording UV–visible absorption spectra were deposited on In_2O_3-coated glass (PPG Industries "Nesatron", 10Ω/square). Film thickness was monitored during deposition by a quartz crystal microbalance (Sloan DTM 200) located adjacent to the sample positions within the bell jar.

The DTM 200 was calibrated by making UV–visible absorption measurments on phthalocyanine films that had been dissolved in concentrated H_2SO_4. The high stability of transition-metal phthalocyanines in concentrated H_2SO_4 has been reported.[58] However, when preparing standard solutions of ZnPc in concentrated H_2SO_4, we observed in some cases a rapid decolorizaton of the solutions. The color stability was not affected by deaeration, addition of small amounts of distilled H_2O, or irradiation by UV light. Stable phthalocyanine solutions could be prepared only by using the following procedure: All glassware was washed with Alconox detergent, rinsed with distilled, deionized H_2O, and rinsed several times with ultrapure concentrated H_2SO_4 (Baker Instra-analyzed). ZnPc (Eastman Kodak) used to make standard solutions was purified by sublimation in vacuo. After weighing, the ZnPc was added to a volumetric flask already containing a large volume (perhaps 10 mL per 1 mg ZnPc) of ultrapure concentated H_2SO_4. Absorbance measurments yielded extinction coefficients of 5.09 × 10^4 M^{-1} cm^{-1} at 204 nm, 7.56 × 10^4 M^{-1} cm^{-1} at 306 nm, 2.06 × 10^4 M^{-1} cm^{-1} at 430 nm, 3.70 × 10^4 M^{-1} cm^{-1} at 697 nm, and 2.37 × 10^5 M^{-1} cm^{-1} at 785 nm. The precision of the absorbance measurements averaged ±0.012 absorbance unit.

All electrolytes were reagent grade and were used without further purification. Aqueous solutions were made with distilled water.

Electrochemical measurements were made on a Princeton Applied Research (PAR) Model 173 potentiostat, a PAR Model 179 digital coulometer, a custom-built digital function generator, and a Houston Model 2000 *x–y* recorder. A saturated calomel reference electrode was used. All electrolyte solutions were adjusted to pH 6.0 ± 0.1 with HNO_3 or NaOH. These solutions were deaerated by bubbling prior to use with N_2 that had first been purified by passing it through a bubbler containing V^{2+}. A nitrogen atmosphere was maintained in the cell during electrochemical measurements.

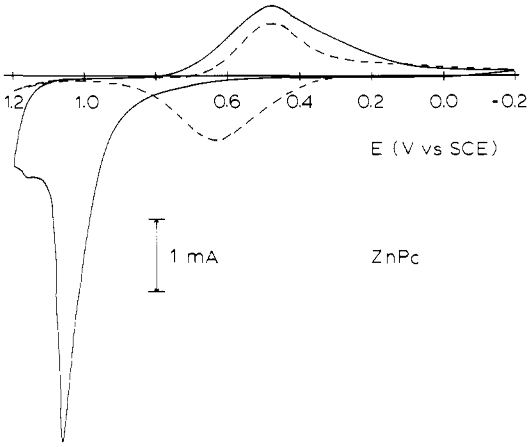

Figure 1. Cyclic voltammogram for ZnPc films (~1600 Å) in 1.0 M $NaClO_4$, v = 100 mV/s: (solid curve) first cycle, (dashed curve) second cycle. Scans begin at negative limit and first move positive. Anodic currents are down; cathodic currents are up.

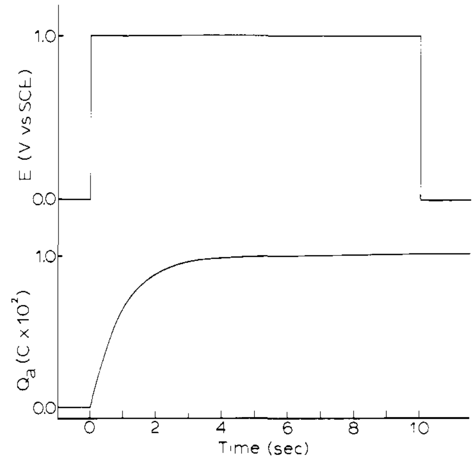

Figure 2. Potential wave form (upper) and anodic charge response (lower) in a chronocoulometric experiment on a ZnPc film (1600 Å) in 1 M $NaClO_4$. Lower curve is for a film that had not been previously oxidized.

UV–visible spectra of phthalocyanine films were recorded by placing the Pc/In_2O_3/glass slides in the light path of a Perkin-Elmer Model 552 spectrophotometer. An In_2O_3/glass slide was placed in the reference beam.

Auger electron spectra were recorded on a Physical Electronics Model 545 Auger electron spectrometer. A 3-keV electron beam at 1 μA was used for excitation (3.6 mA/cm^2). A 1-keV, 25-nA Xe^+ beam was used for ion etching (50 μA/cm^2). The etching rate was approximately 20 Å/min.

Thickness measurements were made on a Varian Å-scope interferometric microscope. Phthalocyanine films were covered with 300 Å of Al for these measurements.

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra were obtained on a Nicolet Model 7199 FTIR spectrometer. The ATR cell used was the ATR Unit TR-9, made by Research and Industrial Instruments Co. This cell contains a KRS-5 internal reflection element and uses a 45° angle of incidence.

Results and Discussion

Electrochemistry. Cyclic voltammetric curves show that ZnPc films undergo a single oxidation and that the oxidized film undergoes a single rereduction (Figure 1). The oxidation peak in the first cycle exhibits a significant overpotential, as compared to the peak position on all subsequent scans. The sharpness of the oxidation peak in the first cycle is indicative of a surface process such as a film restructuring. The oxidation and reduction very likely take place in the phthalocyanine ring, since the Zn center is not expected to offer any electroactivity.

An *n* value for the oxidation of ZnPc was determined by using chronocoulometry. A 10-s potential step (E_{step} = 1.0 V vs. SCE)

---

(57) Faulkner, L. R.; Kahl, J. L., paper presented at the 11th Central Regional Meeting of the American Chemical Society, Columbus, OH, May 7-9, 1979.

(58) Berezin, B. D. *Russ. J. Phys. Chem.* **1962**, *36*, 258.

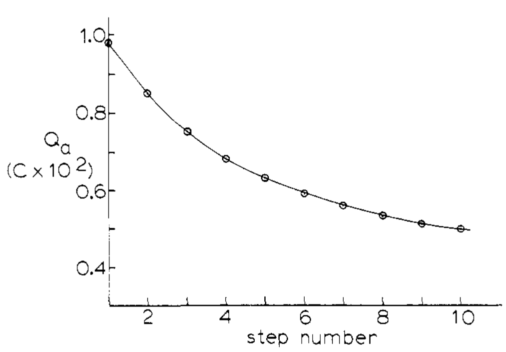

Figure 3. Anodic charge (Q_a) passed during multiple-step chronocoulometry experiment on a ZnPc (~1600 Å) film: E_{init} = 0.0 V vs. SCE, E_{step} = 1.0 V, t_{step} = 10 s, 1.0 M $NaClO_4$.

Table I. Intereferometric Thickness Measurements

thickness,[a] Å	
cycled film[b]	unoxidized film
1200 ± 170	1360 ± 50
1640 ± 140	1530 ± 120
1180 ± 40	1380 ± 40

[a] Data are for three separate samples; each thickness is the average of nine measurements. Error bars give standard deviations of the mean. [b] After 10 oxidation/reduction cycles, ending on reduction.

was applied, during which the anodic charge was measured (Figure 2). The number of moles of ZnPc in identical samples was determined by dissolution of these samples and subsequent absorbance measurements in concentrated H_2SO_4. ZnPc films deposited in positions within the bell jar adjacent to the ZnPc films used for the charge measurements were taken for the absorbance measurements. The resulting *n* value for the initial oxidation of ZnPc films in 1.0 M $NaClO_4$ was 1.21.

Multiple-step chronocoulometric experiments were also performed. Alternating 10-s steps between 1.0 V vs. SCE and 0.0 V vs. SCE were applied. The amount of anodic charge passed during each positive step was recorded. The decrease in charge passed on successive steps is shown in Figure 3.

There are at least two explanations for the observed charge decrease. It is possible that some of the ZnPc is physically removed from the electrode during each oxidation/reduction cycle. However, ZnPc is quite insoluble in H_2O and is so highly colored that if it were lost from the electrode as flakes, it should have been quite evident within or on the surface of the solution. No ZnPc was detected apart from that on the electrode itself. Moreover, interferometric thickness measurements were made on oxidized–rereduced and unoxidized sections of several ZnPc films (Table I). There were no significant thickness differences between the cycled and unoxidized zones. Of course, it is conceivable that upon cycling the films expand and that there is a fortuitous cancellation between expansion and loss of material. However, a 50% change in film density, as would be required if the thickness remained the same while half the ZnPc was lost over typically 10 cycles, seems unlikely. The cycled films might collapse, perhaps upon loss of water, during the deposition of the Al overlayer; but such an effect would not alter the conclusion that the material probably remains on the electrode.

A second explanation for the charge decrease in multicycle experiments is that domains within the films become electrically isolated, perhaps on a grain-by-grain basis. Evidence for this explanation, which we favor, will be presented during the discussion below of results from other experiments.

For the charge balance to be maintained upon oxidation to a level as large as one or two electrons per phthalocyanine site within the films, either positively charged species must exit the film or negatively charged ones must enter. In the case of transition-metal phthalocyanine films, it is the anions from the electrolyte solution that enter the films. Direct evidence for anion uptake will be shown later.

Table II. *n* Values for Initial Oxidations of ZnPc Films

anion	n^a	$r_s{}^b$
NO_3^-	1.24	1.19
ClO_4^-	1.21	1.24
F^-	0.96	1.65
IO_3^-	0.77	2.26

[a] Electrons passed per ZnPc molecule in the film. [b] Darmois, E. *J. Chim. Phys. Phys.-Chim. Biol.* **1946**, *43*, 1.

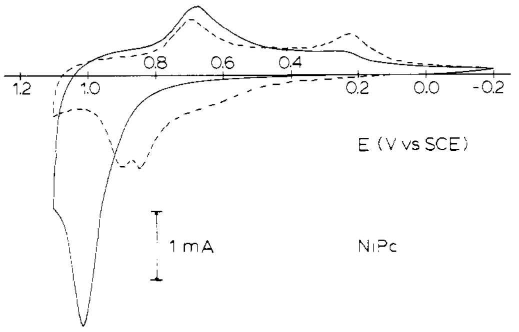

Figure 4. Cyclic voltammogram for NiPc film (~1600 Å) in 1.0 M $NaClO_4$, v = 100 mV/s: (solid curve) first cycle, (dashed curve) second cycle. Scans begin at negative limit and first move positive. Anodic currents are down; cathodic currents are up.

The size of the anions limits their ability to enter the films and thereby limits the rate and extent of film oxidation. Table II contains *n* values for the oxidation of ZnPc in the presence of electrolyte anions of various solution radii. The radii were evaluated earlier by Darmois from conductivities.[59]

FePc, CoPc, and NiPc films differ from ZnPc and CuPc in that they exhibit two couples in their cyclic voltammetric curves. The two oxidation peaks are not always resolved on the first cycle; however, the corresponding reduction peaks are distinct. NiPc films reach a steady state after about 10 cycles (Figure 4), whereas FePc and CoPc cyclic voltammetric curves exhibit a continuous decrease in peak currents. An *n* value of 1.92 was found for the initial oxidation of CoPc using a step potential of 1.1 V vs. SCE. One of the electrons is probably removed from the ring, and the other is probably extracted from the metal center.[11] As mentioned earlier, Gavrilov et al. have speculated that there is an overlap of the voltammetric waves for second ring oxidation and for an oxidation of the metal center in some phthalocyanines.[49] The second ring oxidation was irreversible in their study, and an *n* value for it was not reported. In this study, we have found that the phthalocyanine films flake off the electrode before, or while, a third oxidation process takes place.

Uptake of Anions. The presence of anions in oxidized ZnPc films has been confirmed by Auger electron spectrometry (AES), which has been successfully applied to the study of phthalocyanine films by several workers.[60,61] Typical surface spectra are shown in Figure 5 for two films, one oxidized in KPF_6 solution and the other only immersed in that solution. Both films were rinsed with deionized water after treatment. The presence of fluorine is evident only in the spectrum of the oxidized film.

Since anions are required to balance the charge in oxidized ZnPc films, it is of interest to know how these anions enter the films. The oxidation of the films may proceed in an even front, starting at the film/solution interface and progressing further into the film as greater degrees of oxidation are achieved. The anions would then penetrate along an even front. Alternatively, the oxidation might take place homogeneously throughout the film. The distribution of anions would then be homogeneous at all stages of oxidation.

AES depth profiles were obtained to determine the character of the oxidation process by observing the anion distribution in

---

(59) Darmois, E. *J. Chim. Phys. Phys.-Chim. Biol.* **1946**, *43*, 1.
(60) Buchholz, J. C. *Appl. Surf. Sci.* **1978**, *1*, 547.
(61) Davis, R. E.; Faulkner, L. R. *J. Electrochem. Soc.* **1981**, *128*, 1349.

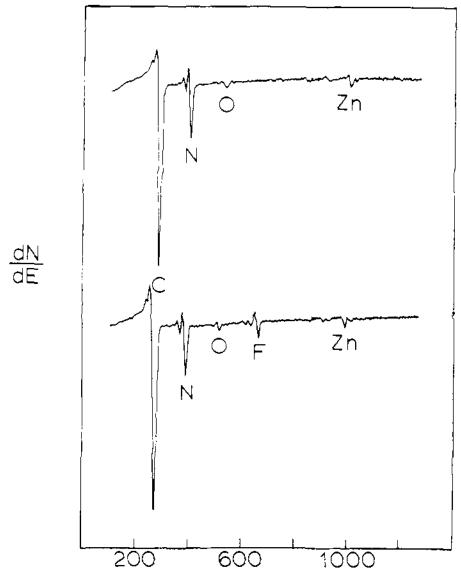

Figure 5. Auger surface spectra: (top) unoxidized ZnPc film, (bottom) ZnPc film oxidized in 0.2 M KPF_6.

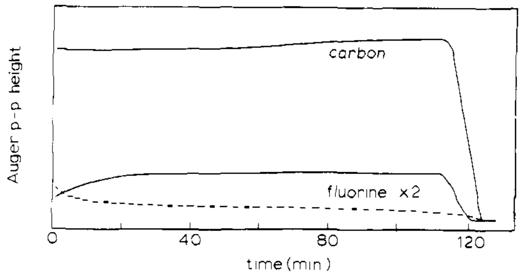

Figure 6. Auger depth profiles for two samples: (solid curve) ZnPc film 88% oxidized in 0.2 M KPF_6, (dashed curve) ZnPc film 23% oxidized in 0.2 M KPF_6. Original thickness of ZnPc was ~1600 Å.

partially oxidized films. Figure 6 contains depth profiles recorded for two ZnPc films, one 88% oxidized and the other 23% oxidized in 0.2 M KPF_6 solution. Only one carbon profile is shown for clarity. Both films exhibit an even distribution of fluorine, which drops to zero at the ZnPc/Au interface.

One must be alert to the possibility that the sputtering beam in the Auger apparatus causes mixing, in the phthalocyanine layer, of sufficient degree to homogenize the distribution of fluorine-bearing species, so that the observed profile appears uniform, even if the original distribution in the sample is not. In earlier work, Davis[61] showed that gross mixing by this mechanism of bilayers of different metal phthalocyanines did not occur. We assume therefore that the fluorine distributions indicated by the depth profiles in Figure 6 do not owe their uniformity to beam-induced mixing. Thus, the results suggest that a frontal penetration of anions does not occur. A reasonable basis for the apparently homogeneous oxidation is provided by the microcrystalline nature of these films. It is known[62,63] that grains in these phases have dimensions of only about 200 Å. Thus there is enormous area on grain boundaries. Given the known rapid diffusion of small species within grain boundaries, it is reasonable to envision oxidation as progressing simultaneously at essentially all grains from the boundaries inward.

Figure 7 contains depth profiles for three other ZnPc films. Comparing the fluorine signal for an oxidized film (curve a) with the fluorine signal for a film that has been oxidized and rereduced (curve b), it is evident that anions leave the film upon rereduction. However, curve b shows that not all of the anions leave, even after the film is held at the reducing potential for approximately 10 min. The retention of anions suggests that oxidized ZnPc remains after the reduction cycle. This observation is consistent with the idea that electrical isolation, probably related to mechanical expansions and contractions of the grains during successive oxidation/reduction cycles, as the cause of decreased charge passage during these cycles.

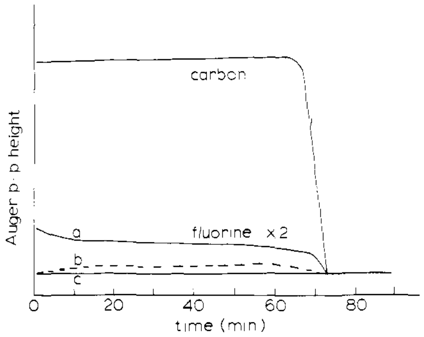

Figure 7. Auger depth profiles for ZnPc films originally ~1000-Å thick: (a) Oxidized in 0.2 M KPF_6; (b) oxidized and rereduced in 0.2 M KPF_6; (c) immersed in 0.2 M KPF_6, but not oxidized. Carbon profile is typical of all three samples.

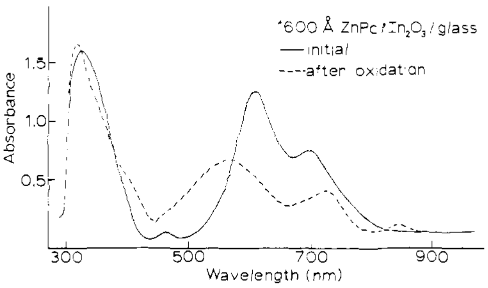

Figure 8. Absorbance spectra of a ZnPc film initially (solid curve) and after first oxidation (dashed curve). Spectra recorded at 1-nm band-pass.

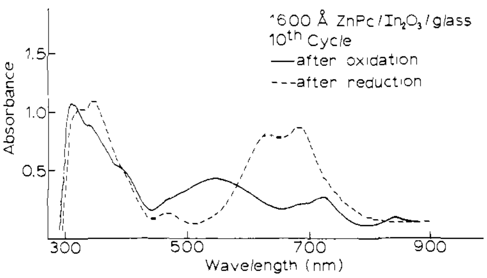

Figure 9. Absorbance spectra of a ZnPc film after 10th oxidation and 10th rereduction. Spectra recorded at 1-nm band-pass.

Table III. Colors of Films on In_2O_3/Glass Substrates

material	original	after oxidation	after rereduction
ZnPc	dark blue	purple	blue
CuPc	dark blue	blue	blue[a]
FePc	dark blue	gray/green	gray/green
CoPc	dark blue	gray	blue/gray
NiPc	dark blue	blue	blue

[a] A shade between the original and oxidized forms.

Electrochromism. Upon oxidation, FePc, CoPc, NiPc, CuPc, and ZnPc films all undergo color changes. Initially, all these materials are dark blue when viewed against the In_2O_3/glass substrate. The oxidized films of different Pc's differ in color (Table III). The rereduced films do not match the original colors. However, for CoPc, NiPc, CuPc, and ZnPc films, the color change appears quite reversible between the oxidized and rereduced colors over many cycles. The color change in FePc is irreversible, even on the first oxidation/reduction cycle.

---

(62) Zhdanov, G. S.; Vorona, Yu. M. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1963**, *27*, 1239.

(63) Katz, W.; Evans, C. A., Jr.; Eaton, D. R.; Faulkner, L. R. *J. Vac. Sci. Technol.* **1978**, *15*, 1561.

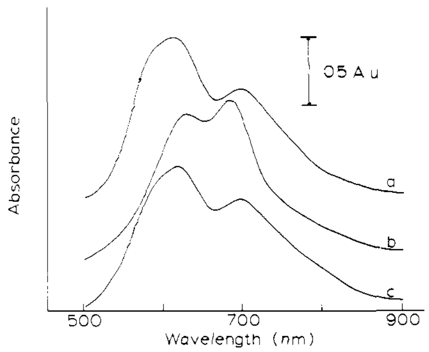

Figure 10. Absorbance spectra for a single ZnPc film originally ~1600 Å in thickness: (a) unoxidized, (b) oxidized and rereduced through one cycle, (c) after heating the oxidized/rereduced form. Spectra are displaced vertically for clarity.

Spectroscopy. The spectral changes that occur upon oxidation of ZnPc films are summarized in Figure 8. The original spectrum is typical of α-phase phthalocyanine films.[25,64] Very little change is seen in the Soret band (320 nm) upon oxidation, but large alterations occur in the region of the peaks originally located at 610 and 700 nm. Figure 9 contains spectra taken on the 10th oxidation/reduction cycle. From the spectrum of the oxidized film, it is evident by the absorptions at 350, 475, and 681 nm that some unoxidized ZnPc remains. The incomplete oxidation of ZnPc films in the later cycles is further evidence for electrical isolation as the cause of charge decrease shown in Figure 3.

After the rereduction of oxidized ZnPc films, the absorption spectrum does not match the spectrum recorded before electrochemical treatment. The relative intensities of the two peaks between 610 and 700 nm are significantly changed (Figure 9), and the splitting between them decreases from 90 to 57 nm. The corresponding peaks in the absorption spectrum of CuPc have been characterized as arising from a Davydov splitting[8,65] manifesting interactions between neighboring phthalocyanine molecules. If the splitting seen in the spectra for ZnPc is likewise due to Davydov splitting, it is clear that the rereduced films involve decreased interaction between adjacent ZnPc molecules by comparison to the original α-phase film. One can probably assume that the spacing between molecules in the rereduced phase is larger than that in the original α-phase. Perhaps some species has entered the film upon oxidation and not left upon reduction. AES results (Figure 7) showed that not all the anions leave upon reduction, but the outcome of the following experiment indicates that these anions are not the cause of the spectral alterations.

After oxidation and rereduction in 1.0 M $NaClO_4$, a ZnPc film was heated in a vacuum oven for 24 h at 125 °C. As is evident from Figure 10, the peak splitting reverted approximately to the original value (80 vs. 90 nm originally). The ratio of the peak intensities also returned nearly to the original value (A_{short}/A_{long}, 1.33 vs. 1.49). Loss of ClO_4^- from the film under these mild conditions is not reasonable.

It is possible that upon oxidation, water enters the ZnPc films along with the anions, and that some of it remains in the rereduced phase. Unlike ClO_4^-, water might be driven off during the heating process. On the basis of infrared specra, Sidorov has concluded the ZnPc does not adsorb water from water vapor.[66] Tachikawa, however, found that ZnPc films, after exposure to water vapor, undergo significant changes in resistivity.[27] Stymne et al. found that after similar exposure, ZnPc films did not undergo an α to β transition upon heating (which occurs otherwise with heat only).[67] These effects indicate that water does interact with ZnPc films.

Attenuated total reflectance Fourier Transform infrared spectra were recorded for films before and after oxidation and after heating as described above. Conclusive evidence for water being present in the films could not be found. The spectra obtained in all cases were consistent with the known IR spectra of α-phase ZnPc films.[68]

Upon oxidation and rereduction, ZnPc films undergo structural changes that are clearly substantial, but that do not restore the original structure and do not rest upon the retention of anions or water in the lattice. The annealing process that takes place upon heating at 125 °C for 24 h converts the film approximately to its original α-phase form. FTIR results show that this process does not involve an α to β transformation.

Similar annealing experiments were done on CoPc films. After heating at 125 °C the rereduced film shows a spectrum that resembles that of the original, unoxidized material more closely than does the unannealed rereduced sample. One might expect that this process of heating would repair rifts in the film that seem to lead to losses of charge-consuming capacity in cycled films. If so, the charge passed during oxidation of these films would be similar to that passed during oxidation of the original film. However, we found that there was no such benefit of annealing.

Concluding Remarks

We have shown here that one can expect compact phthalocyanine films to show a general ability to undergo stoichiometric oxidation, to produce a phase that involves incorporated anions in large numbers, and yet also appears to remain largely intact. It is clear that in applications involving phthalocyanines on electrodes at potentials more positive than 0.9 V vs. SCE, most of them will exist in a ring-oxidized condition. Even at less extreme potentials, phthalocyanies containing an oxidizable metal center may exist on the electrode in a charge-compensated phase with the metal center fully oxidized, while the ring remains reduced. Our experiments suggest that the oxidized materials are good electronic conductors, but we have no direct information on this point.

Acknowledgment. We are grateful to the Department of Energy, Division of Materials Sciences, for supporting this research under Contract DE-AC02-76-ER01198, administered by the Materials Research Laboratory of the University of Illinois.

Registry No. Zn(Pc), 14320-04-8; Cu(Pc), 147-14-8; Fe(Pc), 132-16-1; Co(Pc), 3317-67-7; Ni(Pc), 14055-02-8; NO_3^-, 14797-55-8; ClO_4^-, 14797-73-0; F^-, 16984-48-8; IO_3^-, 15454-31-6; $NaClO_4$, 7601-89-0; KPF_6, 17084-13-8.

---

(64) Lucia, E. A.; Verderame, F. D. *J. Chem. Phys.* **1968**, *48*, 2674.

(65) Abkowitz, M.; Monahan, A. R. *J. Chem. Phys.* **1973**, *58*, 2281.

(66) Sidorov, A. N. *Opt. Spectrosc.* (*Engl. Transl.*) **1962**, *13*, 379.

(67) Stymne, B.; Sauvage, F. X.; Wettermark, G. *Spectrochim. Acta, Part A* **1979**, *35A*, 1195.

(68) Sidorov, A. N.; Kotlyar, I. P. *Opt. Spectrosc.* (*Engl. Transl.*) **1961**, *11*, 92.