I. SYNTHESIS AND PHYSICAL CHARACTERIZATION OF SELECTED POLYSTYRENE SUPPORTED PHTHALOCYANINE COMPLEXES

II. ELECTRON TRANSFER STUDY BETWEEN TITANOCENE DICHLORIDE AND REDUCED TITANOCENE DICHLORIDE ANION

By

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A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirement
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1982

ABSTRACT

I. SYNTHESIS AND PHYSICAL CHARACTERIZATION OF SELECTED POLYSTYRENE SUPPORTED PHTHALOCYANINE COMPLEXES

II. ELECTRON TRANSFER STUDY BETWEEN TITANOCENE DICHLORIDE AND REDUCED TITANOCENE DICHLORIDE ANION

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I.

For the past four decades the rather weak catalytic activity of phthalocyanine complexes toward oxidation process has been known. As a class, the compounds are inexpensive and widely available due to their use as fabric dyes. The limitation to their catalatic activity was claimed to be caused by dimer formation between phthalocyanine groups.

Recently due to interest in the isoelectric porphyrin system role in biologic oxidation reactions, work has been renewed on the structually similar phthalocyanines. To be active in oxidation processes these systems rely on site isolation of individual metal ligand complexes. Such a system is reported here.

Nickel, vanadyl, cobalt, iron, and manganese phthalocyanine compounds have been attached to polymers by binding the chlorosulfonated metal phthalocyanines to styrene divinyl benzene (20% and 8% divinyl benzene) copolymers. Attachment by direct sulfonylation and by

formation of the sulfonamide linkage were carried out. Physical characterization of the resulting complexes was accomplished by electron spin resonance analysis, transmittance electron microscopy, scanning electron microprobe analysis, and differential scanning calorimetry. The effect of the presence of the polymer resin based complexes in contact with cyclohexene during its oxidation are reported in detail. Additional oxidation reactions with these complexes were attempted with 1- and 2- octene, toulene, and cumene.

II.

Biscyclopendadiehyl titanium dichloride (titanocene dichloride) has been reduced with aluminum to give a reduced Ti(III) compound with a pronounced electron spin resonance spectrum. The reduced Ti(III) complex was treated with the parent titanium (IV) complex of titanocene dichloride in tetrahydrofuran. Linewidth broadening of the ESR spectrum allowed calculation of the rate of electron transfer between the Ti(IV) and Ti(III) metal complexes as $k=2.3 \times 10^{8} M^{-1} sec^{-1}$.

ACKNOWLEDGMENTS

The author would like to thank Dr. C. H. Brubaker and the graduate students of his research groups. Special thanks go to Beth McCulloch, Fred Batzer, and T. Tomi Li.

The assistance of the mass spectrotometry, electron microscope, and microprobe analysis laboratories of Michigan State University is gratefully acknowledged.

Very special appreciation is expressed to my family for their continuing support in my many years of graduate studies.

The editorial and typing skills of Mrs. Christine French earn a special note of thanks for the many trials and revisions made in this manuscript.

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CHAPTER I

INTRODUCTION

A. Introduction to Catalysts

Classically catalysts are grouped into two categories, distinguished from each other by the physical state of the catalytic compound and the substrate upon which it acts. Those which dissolve in a reaction medium in which a substrate also dissolves are termed homogeneous and those which remain undissolved in the solvent are called heterogeneous or "contact" catalysts. Each group has certain advantages and disadvantages when used in reaction mixtures. Homogeneous compounds tend to be more efficient and operate at lower temperatures and pressures,[1] and tend toward more selectivity to particular substrates. Heterogeneous catalysts are dependent upon mechanical factors such as how well the system exchanges fresh substrate and brings it into contact with the undissolved catalyst surface. The number and type of true heterogeneous catalysts available are limited to a small set of expensive metals, such as platinum and palladium. The contact catalysts show similar reactivity toward substrates and, therefore, display distinct selectivity limitations. However, the physical nature of the heterogeneous catalysts results in isolation of the compounds in a physical phase distinct from that of

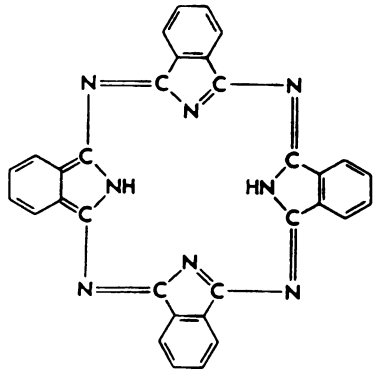
the substrate upon which it acts. Thus, it facilitates separation of reaction product from the catalytic reagent.

The desire to produce a hybrid-phase catalyst, that is a complex which displays advantages of both heterogeneous and homogeneous systems, has led to the development of compounds where an insoluble support replaces one or more ligands on an active metal center.[1,2] Grubbs[1] gives an extensive review of various types of supports and catalysts available and suggests a classification of hybrid-types based upon mode of ligand attachment to the metal centers. He also discusses matrix imposed selectivity changes which result from mechanical limitation of the insoluble support.

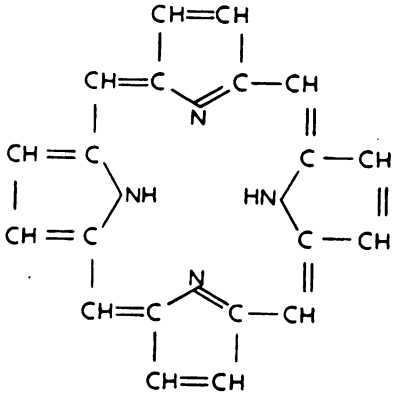
Thus, in theory, judicious choice of support material, catalyst, and hybridization mode (attachment) should result in production of specific catalysts to use with specific substrates.

B. Introduction to Phthalocyanine Compounds

Phthalocyanines are man-made macrocyclic compounds which are isoelectronic with the naturally occuring porphins (Figure 1). Early investigators recognized that metal phthalocyanines displayed the ability to slightly enhance oxidation processes,[3,4] and for some time much research effort was put into their use. However, due in part to



Phthalocyanine



porphin or
porphyrin (II)

Figure 1. Comparison of Structures of Phthalocyanine and Porphyrin

the low reactivity which contemporary researchers attribute to the formation of oxygen bridged metal phthalocyanine dimers,[5] these efforts waned in all but a few specific areas. Review of recent literature reveals that much of the current interest in the catalytic behavior of phthalocyanines involves their use as "sweetening" agents in petroleum. In that role they are used to remove mercaptans and other sulphur containing compounds by oxidation.[6-11]

Other areas of current interest are vapor phase reactions[12,13] and biologic enzyme modeling by manganese phthalocyanine.[14]

C. Supported Phthalocyanine Compounds

The expansion of work performed on the oxygen carrying ability of the metal porphine systems[15] and their known "site" isolation in biological systems gives new impetus to study methods of support of the phthalocyanines.[5]

Without attachment to a non-dissolving support it is possible to use the phthalocyanines as homogeneous or heterogeneous catalysts by simple choice of reaction solvent. Likewise, aromatic substitution of the macrocycle will result in a change of its solubility characteristics. Such choice of reaction conditions do not, however, result in site isolation of the metal complex.

Therefore, it is better to examine the procedure of supporting phthalocyanines for subsequent reactions not as simply "heterogenizing"

them but rather as attempting to control the environment about the metal centers in order to increase reactivity toward a specific system. Such systems would require rigid covalent attachment to bind the phthalocyanine groups to an inert support at specific locations. In doing so, not only is heterogeneity preserved, but also it should then be possible to control environmental factors which result in dimer formation of the metal phthalocyanine complex[5] (Figure 2).

Zwart and co-workers describe such a system in their preparation of covalently attached cobalt phthalocyanine-polymer systems.[5] Their method of attachment to the polymer involves chloromethylation of the polymer and then amination so that cyanuric chloride can be used as a coupling agent to aminated cobalt phthalocyanine (Figure 3).

The degree of specificity which a particular attached catalyst system will show toward any given substrate should, in theory, be controlled to an even greater extent by the matrix environment which the substrate must penetrate to reach the catalytic metal centers. Ideally such systems would contain insoluble supports, which, by their physical nature, prevented or enhanced the ability of the substrate to pass through it to specifically located catalytic centers. Of necessity such conditions could only be provided by custom synthesis of the support. In fact, in order to prepare systems in which the number and placement of active metal centers were exactly known, it would be

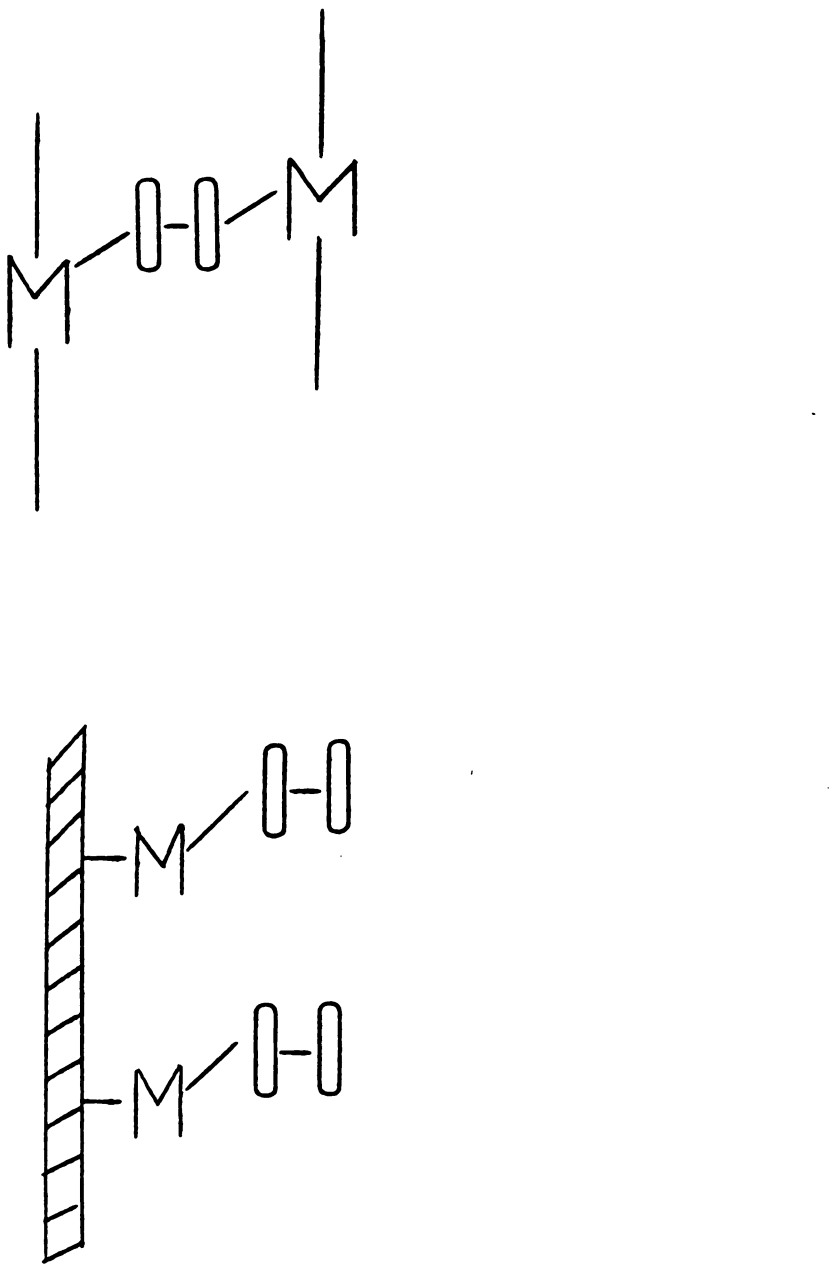
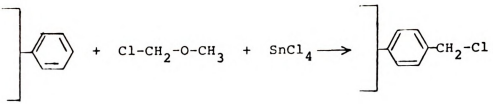
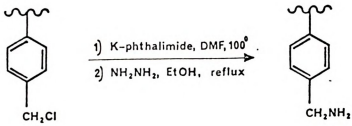
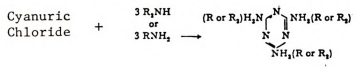


Figure 2. Dioxygen Bridged Phthalocyanine Dimer and Dioxygen Monomeric Phthalocyanine on Polymer Support





i cyanuric chloride coupling of amines:
(Aminated polymer + aminated phthalocyanine)



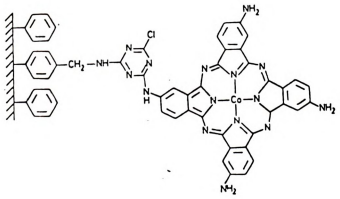


Figure 3. Cyanuric Chloride Coupling Method to Support Phthalocyanines on Polymers

necessary to produce well defined polymers from monomers to which the catalyst had previously been attached. Such systems are known for the phthalocyanines, research being provided on similar systems for the manufacture of dyes. However, such intricate work with the nature of the polymerization process itself is beyond the scope of the study undertaken here, which has as its primary thrust the attachment of phthalocyanines on commerically obtained polymers and subsequent characterization of the resulting compounds.

D. Introduction to Specific Polymer Supported Phthalocyanine Research Carried Out

The original intention of the research reported here was to compliment ongoing research performed in the past in Dr. Brubaker's groups[16,17,18] and Dr. Grubb's group[19,20] by supporting a new class of compounds on polystyrene support which would later be used as catalysts. Since it was desired to anchor the phthalocyanines solidly to the polystyrene matrix the methods of sulfonylation and sulfonamide formation were chosen so that a covalent linkage would form between the ligand and the polymer support. The former method results in a sulfone linkage which is a rather stable bond and both methods result in a linkage which has a shorter side chain than that of the cyanuric coupling method used by Zwart.[5] The length of this side chain seemed critical since prevention of dimer formation was one of the goals of

the research. In addition, since the phthalocyanine group was multiply substituted in the chlorosulfonation step, it was thought necessary to keep the side chain short so that the degree of additional cross linkage through multiple attachment of each phthalocyanine molecule was held at a minimum.

After the initial experiments it was clear that the degree of "loading" of phthalocyanine onto polymer was low and that the surface of the beads seemed to react but the interior of the beads remained unreacted to sulfone or sulfonamide linkage. Therefore, many experiments followed in which reaction time, temperature, and solvent were adjusted in an attempt to increase the linkage formation. Surprisingly solvent was of little effect and time and temperature change the loading only very slightly. By accident, in one experiment, a sample of beads was crushed by the stir bar and so, thus exposed to additional reactive surface, the sample was seen to take up much more phthalocyanine reactant. Therefore, it was reasoned that some blockage was occuring during the initial reaction of the bead at its surface with the phthalocyanine reactant. Concurrent experiments with oxidation reactions of the prepared phthalocyanine beads with organic substrates were disappointing because the reactions showed little or no increase in reaction rate above that of the unsupported phthalocyanine-organic substrate mixtures, and so apparently the site isolation of the metal centers was not being fully realized.

Thus, because of the difficulties with synthesis and use of these

compounds, a detailed characterization of the beads was carried out using scanning electron microprobe analysis, electron spin resonance, transmittance electron microscopy, and differential scanning calorimetry. Results appear in Chapters III and IV.

CHAPTER II

EXPERIMENTAL

A. Preparation of Chlorosulfonated Metal Phthalocyanines

Following the chlorosulfonating procedure outlined by Moser and Thomas[4] or Booth[3] in their reviews of phthalocyanine compounds, the tetrasubstitution of the metal phthalocyanine compounds was carried out simply by dissolving the materials in chlorosulfonic acid and heating them to 125°C. The reaction products were then separated from the excess chlorosulfonic acid solvent by vacuum distillation and the substances thus recovered were used in subsequent polymer sulfonylation steps without further purification.

Although the amounts of phthalocyanine and chlorosulfonic acid solvent varied throughout the research, a general procedure was developed as follows:

2.25 g of Nickel phthalocyanine (Eastman lot number A2E) or vanadyl phthalocyanine (Eastman lot number A7A) was placed in a 200 mL three-neck round bottom flask fitted with a water condenser, magnetic stirring bar, and thermometer. Thirty mL of chlorosulfonic acid was pipetted into the flask and the mixture heated to 125-135°C overnight. The flask was continuously flushed with nitrogen to maintain an inert

atmosphere. The excess chlorosulfonic acid was removed by vacuum distillation leaving behind a thick, highly colored oil of chlorosulfonic acid contaminated tetrasulfonated metal phthalocyanine complex.

The ratio of metal phthalocyanine to chlorosulfonic acid varied for the experiments in which cobalt phthalocyanine and iron phthalocyanine were the complexes upon which substitution was carried out. Unfortunately due to their lack of adequate stability in the strong, acidic solvent, the resulting products proved at best to be marginally successful in the following sulfonylation steps. (See Chapter III).

Finally it should be noted that the length of time which was allowed to complete the chlorosulfonation was in great excess of the two to three hours suggested by Moser and Thomas[4]. The reaction time was so chosen to insure that the subsituted metal phthalocyanine was indeed tetra substituted for, as Booth points out, [3] control of time and temperature results in selective substitution of the macrocycle at from one to four positions. Further, Booth makes the point that chlorosulfonation carried out by the preceding method results exclusively in 3-substitution.

B. Preparation of Polystyrene-DVB Copolymer Beads

The 20% divinylbenzene-polystyrene copolymer beads used as the solid support are commercially available and were gifts from the Dow Chemical Company. Prior to their use in sulfonylation reactions with

chlorosulfonated phthalocyanines they were sieved through standard 28-32 mesh screens (0.0234-0.0197 in.). Then they were washed with the following solvents: 10% HCl, 10% NaOH solution, water, 1:1 water/methanol, methanol, 1:1 methanol/dichloromethane, dichloromethane. The beads were then dried under vacuum.

C. Sulfonylation of Polystyrene-DVB Copolymer Beads with Metal Phthalocyanines

The choice of sulfonylation conditions resulted from suggestions by Olah in his review of Friedel-Crafts type reactions.[21] Nitromethane was chosen as the solvent for the reactions and aluminum chloride as the sulfonylation catalyst. The beads resulting from the first experiment varied so much in color and, thereby, their presumed loading of metal complex on polymer support, that an entire series of reactions were undertaken in which amounts of chlorsulfonated metal phthalocyanine, aluminum chloride, or polymer were varied. (See Chapter III). Finally a general procedure was developed for the two sulfonylation products which were later tested for catalytic activity. The following procedure was typical:

The 200 mL round bottom flask that contained the chlorosulfonated metal phthalocyanine (either nickel or vanadyl phthalocyanine) was refitted with a mechanical stirrer in addition to a condenser and thermometer. Ninety mL nitromethane and 2.25 g aluminum chloride were added. The solution was stirred until most of the oily chlorosulfonated metal phthalocyanine had dissolved. Then 15 g 20%

DVB-polystyrene copolymer beads was added and the solution heated to 45-50°C. The solution was stirred for 48 h under nitrogen. The nitromethane was removed by suction filtration and the beads were then washed with 1) nitromethane, 2) methanol, 3) water, 4) methanol, and 5) dichloromethane. The beads were then floated in a separatory funnel containing dichloromethane 4 to 8 times and those beads and other extraneous materials that sank were removed. The beads were allowed to dry in the air. The beads were transferred to a Soxhlet extraction apparatus and extracted with methanol for 70-72 h. The final extraction solvent was checked by visible spectroscopy and revealed no trace of excess unreacted metal phthalocyanine. The beads were dried in a vacuum at 55-67°C.

D. Preparation of Substituted Nickel and Vandayl Phthalocyanine Standards

So that oxygen uptake and catalytic oxidation studies of the polymer attached metal phthalocyanine compounds could be compared to identical, non-supported metal complexes, tetrasubstituted nickel and vanadyl phthalocyanine-sodium sulfonate were made by the following prodedure:

0.2 g metal phthalocyanine was placed in a round bottom flask fitted with condenser, magnetic stirrer, and thermometer. 2.66 mL of chlorosulfonic was added. The mixture was stirred under nitrogen at 115-118°C for 19 h. The solutions were hydrolysed by pipetting them over ice. The resulting water solution was neutralized with sodium

bicarbonate until production of carbon dioxide ceased. The solution was filtered out then placed in dialysis tubing (Union Carbide size 36 DM), which had been previously prepared by boiling it in water for 15-20 min and then rinsing it with water. The filled tubing was placed in a 2000 mL beaker filled with water and the water was stirred for 3 h before the dialysis tubing was changed and the process repeated for an additional 3 h. The water was changed twice during the next 11 h but the dialysis tubing was not changed. A small sample of the solution remaining in the dialysis tubing was checked for SO^{2-} and CO^{2-} with barium chloride. The solution contained in the dialysis tubing was then allowed to air dry in an open beaker to yield the final product.

E. Preparation of Chlorosulfonated Nickel, Iron, Cobalt, and Manganese Phthalocyanines for Sulfonamide Reactions

These reactions are nearly identical to those carried out for the standards above. Typically, the appropriate metal phthalocyanine (1.5 g) was treated with chlorosulfonic acid (20 mL) at elevated temperatures 120-130°C for 1 1/2 h. Then the solution was hydrolyzed over ice and neutralized with Na_2CO_3 (40 g). The resulting solution was filtered into dialysis tubing (Union Carbide 36 DM) and so purified overnight in about 6 L of distilled water. The solution remaining in the dialysis tubing was evaporated to dryness. Before use, the compounds so formed were treated with thionyl chloride at reflux for 4 h and then isolated by vacuum distillation.

F. Preparation of Aminated Polystyrene-Divinylbenzene Copolymer[7]

10 g of 20% (or 8% in other reactions) divinylbezene-polystyrene beads was treated with 38 mL acetic anhydride, 8.4 mL acetic and 3 mL nitric acid and the solution stirred under N_2 for 5-14 h depending on amount of reaction desired. They were isolated and washed by stirring in five portions of acetic acid for 15 min each. Then 40 mL acetic acid was added with 12 mL of HCL and 11 g of $SnCl_2 \cdot 2H_2O$ for the reduction of $-NO_2$ groups to $-NH_2$. The solution was stirred at 40^oC for 2 d, 22.5 h. The aminated beads were washed by stirring with a 3:10 mixture of HCl:acetic acid (5 portions, 15 min each). Then they were washed with a mixture of 3:5:5 HCl:THF: Methanol (15 min each, 3 times) and then twice with methanol. The beads were dried at room temperature and then treated before use by washing two times with 10% methanolic KOH, then 5 times with methanol and twice with methylene chloride. Finally, the beads were vacuum dried at least 4 h.

G. Preparation of Copolymer Attached Nickel, Iron, Cobalt, and Manganese Phthalocyanines by Sulfonamide Linkage

0.175 g of the appropriate chlorosulfonated metal phthalocyanine was stirred in a chlorinated solvent (chloroform, methylene chloride) or nitromethane along with 0.5-1 g of aminated beads. Some reactions were carried out at higher temperatures (80-90^oC) although there seemed to be little effect of temperature on the final product. In a few

cases triethylamine was added to the mixture and some effect was seen upon its addition (see results of SEM below). The beads were isolated and washed with, typically, chloroform, methylene chloride, methanol, water, and methylene chloride. They were floated in methylene chloride in a separatory funnel to remove any heavy unreacted particulate matter and then Soxhlet extracted with methanol before being vacuum dried.

H. Equipment for Analysis and Physical Characterization

Thermal analysis by differential scanning calorimetry was carried out on a DuPont Model 990 thermal analyzer. Electron spin resonance was done by use of a Varian 4502 X-band instrument equipped with a Micro-Now gauss meter and a Hewlett Packard X532B frequency meter. The transmittance electron microscopy was performed with a Philips 300 electron microscope and the scanning electron microprobe analysis utilized an Allied Research Laboratory (ARL) EMX-SM spectrometer.

I. Elemental Analysis

The elemental analysis of supported phthalocyanines was carried out by the scanning electron microprobe as this method proved more precise than trace elemental analysis by commercial atomic absorption. The method compared the x-ray count rate of the metal in the compound of interest to the count rate of the pure element for the metal in question. Results appear in Table I.

The beads were not uniform in loading (see section on scanning

TABLE I Elemental Analysis of Bound Metal Phthalocyanine Polymer Complexes

Supported Polymer Complex	% Metal Measured at Surface of Bead	% Metal avg. Entire Bead	mmole of Metal for Entire Bead in Reaction per 0.1 g beads
Ni Sulfone linkage	0.06	0.011	1.87×10^{-4}
VO Sulfone linkage	Same as whole bead*	0.0027	5.30×10^{-5}
Co Sulfonamide linkage	0.165	0.024	4.07×10^{-4}
Fe Sulfonamide linkage	0.163	0.035	6.63×10^{-4}
Ni Sulfonamide linkage	0.03	**	-----
Mn Sulfonamide linkage	**	**	

*Very low loading

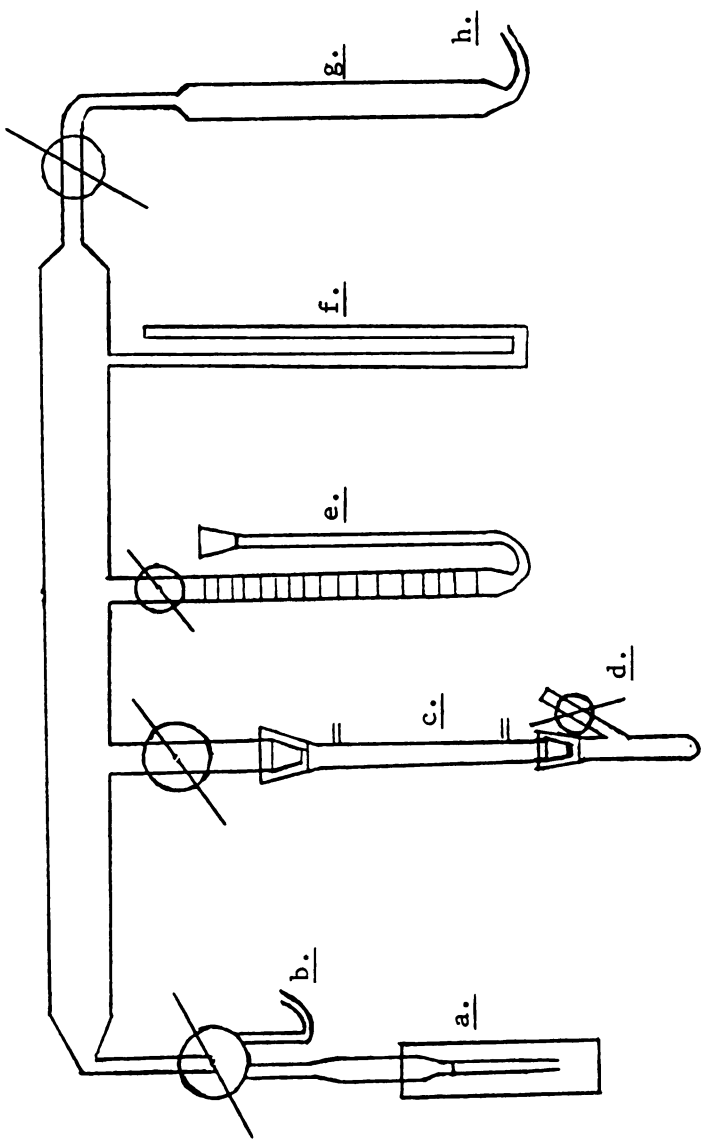
**Count rate a background level. (See Text)

electron microprobe below), therefore, it is necessary to average the count rate to determine the average percentage of metal in any particular sample.

J. Oxygen Uptake of Various Organic Compounds Catalyzed by Metal Phthalocyanines

An oxygen uptake manifold was constructed which provided a means of supplying oxygen to a vessel containing the catalyst and organic compound upon which the oxidations were to be carried out, Figure 4. As attending apparati, there were a mercury manometer, which actually was of little use in the experiments reported here, a mercury filled gas buret with leveling bulb, an oil bubbler device fitted with a marked dip tube with which it was possible to maintain manually the pressure inside the manifold at atmospheric pressure, and a gas drying tower through which oxygen was introduced into the system.

A typical oxygen uptake experiment was conducted as follows: 0.1 g of supported metal catalyst was placed in the reaction vessel with a magnetic stirring bar and the vessel, connected to a water condenser, was attached to the oxygen manifold. An oil bath heated by a nichrome immersion coil and stirred by a mechanical stirrer was placed about the reaction flask so that a chosen temperature for the reaction could be maintained (Either 50-60^{o}C or more commonly 75-85^{o}C). 3 mL of organic solvent-reactant was injected into the reaction vessel which had previously been evacuated and refilled with oxygen through the



a. oil bubbler
b. vacuum
c. water condenser
d. sample
e. gas buret
f. mercury manometer
g. gas drying tower
h. oxygen inlet

Figure 4. Manifold for Oxygen Uptake Studies

Figure 4. Manifold for Oxygen Uptake Studies

manifold. The solution was stirred throughout the course of the oxygen uptake study which varied from approximately 6 h for the more effective catalysts at higher temperatures to 48 h for the less reactive and lower temperature studies.

In some cases the catayst beads were isolated from the reaction mixture washed with fresh portions of solvent and quickly dried under vacuum. The reaction conditions were reestablished and a second run carried out using fresh organic reactant. (Chapter III).

The tetrasubstituted metal phthalocyanine-sodium sulfonated standards were studied in a similar manner with the exception that the amount of catalyst used in the experiments was determined by computing the amount of catalyst present in the beads from elemental analysis (as weight of metal in grams), performed commerically, by Schwartkopf Microanalytical Laboratory; and taking a corresponding amount of non-supported catalyst. Since these typically were very small amounts, it was necessary to take up a given sample of non-supported catalyst in water, make a standard solution in a volumetric flask and pipet an appropriate amount into the reaction flask. The water was allowed to evaporate from the solution leaving the standard catalyst which was then used in the oxygen uptake studies.

K. Catalytic Oxidation Studies Without Measurement of Oxygen Uptake

1. Reaction Conditions

A less eleborate oxygen manifold was constructed that allowed

three reaction vessels to be used at once. It maintained internal oxygen pressure by allowing an excess flow of oxygen to pass continuously through its oil bubbler. Once again an oil bath-heater system was used to control reaction temperature. Reaction conditions were chosen so that 0.1 g of supported catalyst or its equivalent in standard non-supported catalyst was stirred in 3 mL of reactant-solvent which were the organic compounds (cyclohexene, 1-octene, 2-octene, toulene, cumene) upon which oxidation was attempted. The vessels were attached to water condensers, which were hooked to the oxygen supply manifold. The reactions were long-term, lasting for a typical time of 47 h. The reaction mixtures resulting from the procedure were separated from the catalyst; the catalyst, were washed in isopropanol and stored.

2. Analysis of Products

The reaction products were analyzed by gas chromatography by using a Varian Aerograph Model 920 Chromatograph with thermal conductivity detector. An SE-30 column proved to be effective in separating the components of the mixture. It was 10 ft long by 1/4 in in diameter and contained 10% SE-30 supported on WHP. Column temperatures varied from 50-100^{o}C depending on the particular use of the device and the nature of the reaction mixture. Amounts of each component were determined by the integration device on the recorder. In one case, that of cyclohexene, the nature of one component was confirmed by Michigan State University's Biochemistry Department Mass Spectrometry Facility by using a coupled gas chromatograph/Mass spectrometer.

CHAPTER III

PHYSICAL CHARACTERIZATION OF POLYSTYRENE SUPPORTED METAL PHTHALOCYANIENES

A. Differential Scanning Calorimetry

Due to failure of the thermal analyzer only the first samples of the sulfonylation reactions were analyzed by DSC. The results appear in Figure 5.

The figure shows that the bead has changed thermal characteristics after treatment with a metal complex. The low loading (very low due to sulfonylation attachment, see next chapter) of the cobalt species is only slightly different from the parent polystyrene but does show a shifting of its exothermic transitions. The difference for the nickel complex is dramatic. The transition between 100-175°C is greatly broadened from that of the parent. The transition corresponds to the decomposition of the polystyrene (Polystyrene does not melt cleanly even in the nitrogen atmosphere of the DSC cell). The most likely process responsible for such an observation is that additional crosslinkage between polymer chains is taking place with the availability of multiple sulfonylchloride groups on each of the metal

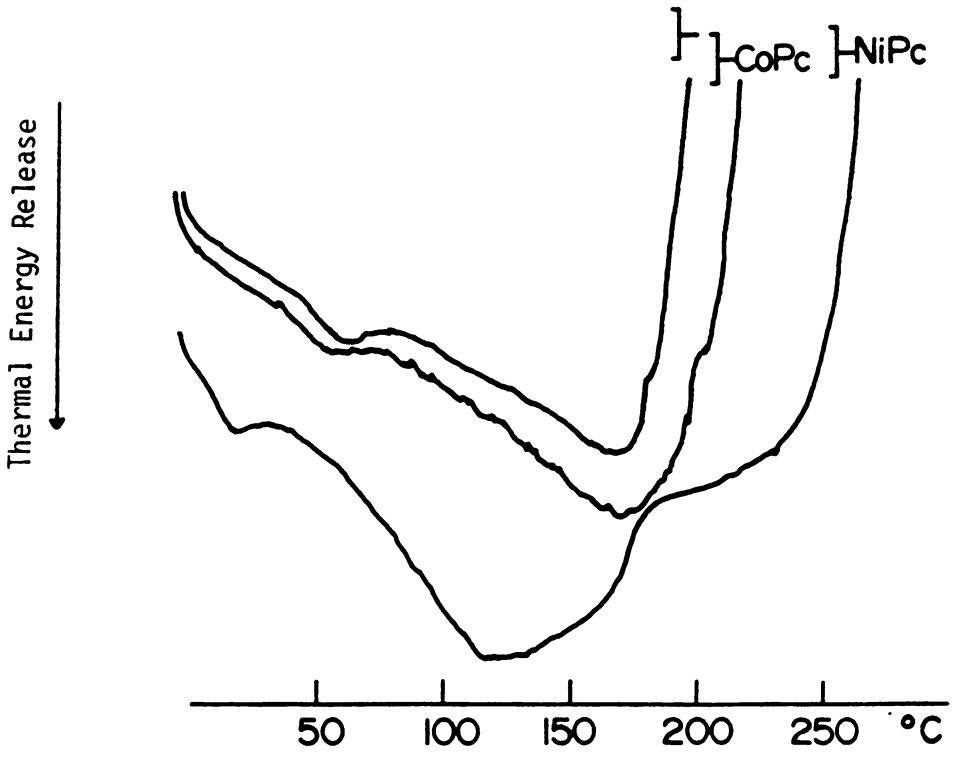


Figure 5. Differential Scanning Calorimetry Traces of 20% Divinyl-Benzene Polystyrene, Cobalt and Nickel Phthalocyanine Bond 20% Divinylbenzene Polystyrene.

centered phthalocyanine molecules. In fact, a qualitative difference between highly reacted polystyrene beads and their unreacted counterparts was noted in the cutting process in sample preparation necessary for scanning electron microprobe analysis. An increased surface hardness was noted in the reacted beads. This also is most likely due to a degree of cross linking by the metal complex during reaction.

B. Electron Spin Resonance

ESR data were unsurprising. Figure 6 shows the spectra of the vanadyl complex made by the sulfonylation method and the manganese complex with the sulfonamide linkage. Both spectra are as expected. Vanadyl has a spin number, I = 7/2, and shows the expected 8 line spectum. Likewise the Mn(II) complex is 5/2 and displays 6 lines in its spectrum. Spectra for iron and nickel were not obtained indicating Fe(II) and Ni(II) were present. Cobalt displays somewhat unexpected behavior. Lack of an ESR signal suggests that the cobalt has possibly been oxidized to Co(III) from the expected Co(II) state during complex formation. However, cobalt spectra are difficult, at best, to obtain with supported species on the polystyrene matrix.

The only other feature of note is a strong singlet at a g value near free spin. This line is seen in all samples prepared by sulfonamide linkage and is also present in unreacted amino polystyrene beads made by the method outlined in the preceding chapter. Multiple attempts were made to rid the samples of the extra signal but in all

Figure 6. Electron Spin Resonance Spectra of 20% Divinylbenzene Polystyrene Bound Complexes of Manganese and Vanadyl Phthalocyanine.

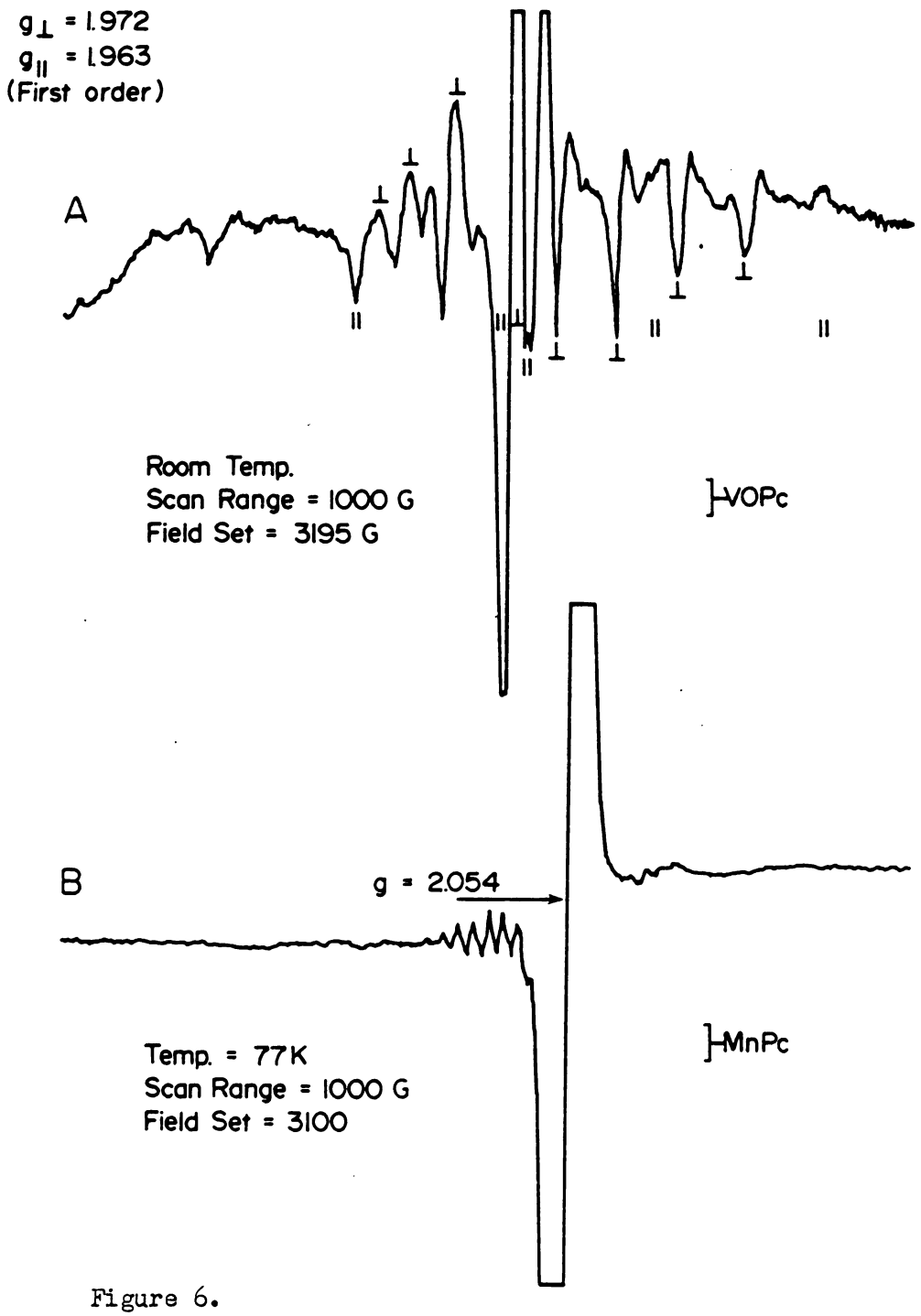

$g_\perp$ = 1.972
$g_{||}$ = 1.963
(First order)
A
Room Temp.
Scan Range = 1000 G
Field Set = 3195 G
VOPc
B
g = 2.054
Temp. = 77K
Scan Range = 1000 G
Field Set = 3100
MnPc

Figure 6.

preparations the signal persisted apparently due to the same radical formation on the amino polystyrene during its preparation.

C. Transmittance Electron Microscopy

The samples were prepared by embedding the polymer beads in epoxy resin and taking ultra-thin sections. Figure 7 shows a photomicrograph of both 8% crosslinked divinylbenzene-polystyrene and 20% divinylbenzene-polystyrene at 40,000X magnification. The 20% sample contains cobalt phthalocyanine. In addition Figure 7 shows two other photographs at the edge of a phthalocyanine reacted bead at 32,000X and 52,000X magnification. From the micrograph the size of the open structure of the bead can be seen, hence, because samples were all 20% DVB-polystyrene copolymer in the catalytic experiments, it is interesting to note that in these cases the channel size is approximately 500 times the diameter of a phthalocyanine molecule. However, as is seen in the reacted sample in Figure 7c the beads surface appears practically occluded at the surface. Unfortunately, the fine resolution of the electron microscope would not allow the certain determination that high surface loading would preclude entrance of other phthalocyanine reagent into the interior of the bead. The TEM evidence coupled with the scanning electron microprobe data (see below) indicates that the phthalocyanines attach themselves at available sites at the polymer surface and that such attachment then interferes with penetration of the remainder of the reactant to the interior of the bead.

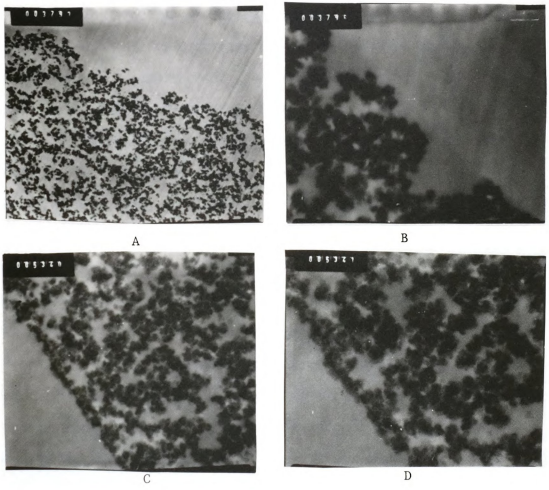


Figure 7. Electron Photomicrographs of A) 8% Divinylbenzene polystyrene at 3200X, Cobalt Phthalocyanine Attached to 20% Divinylbenzene polystyrene at B) 40000X, C) 32000X, and 52000X.

D. Scanning Electron Microprobe Analysis

In scanning electron microprobe analysis a narrow beam (0.3 micron diameter) of high energy electrons (10-25 kV) is swept across a cross-section of a sample bead. X-rays characteristic of the elements present in the sample are produced from a 1 to 10 micron diameter volume. The instrument provides a detector which is usually set to receive the K_{α} line of the element in question. Count rate as a function of beam sweep is plotted-typical graphs appear in Figure 8 and the Appendix. Therefore, the graph represents amount of a particular element at any particular position along the sweep of the electron beam. The samples were prepared by slicing the beads with a razor blade while attempting to section them as close to the center of the bead as possible. The bead sections were mounted on a carbon target with two sided rubber tape and the target and sample then were coated with carbon in a high vacuum evaporization apparatus. The coating is necessary to insure adequate conductance of the sample.

In all cases the results are similar. A high degree of loading of the phthalocyanines is achieved at the bead surface but a sharp and dramatic drop off occurs in loading toward the center of the beads. Even in experiments with extended reaction time and in the presence of an amine scavenger (triethylamine) to pick up the HCl produced during the coupling reaction no large improvement is seen (Figure 8b). To be sure, the excess time of treatment and higher temperature at which the reaction was run (27 h and reflux temperature of 1,2 dichloromethane)

Figure 8. Scanning Electron Microprobe Analysis of Phthalocyanine Reacted 20% Divinylbenzene Polystyrene (A & B). Comparison SEM of Cobalt Porphyrin Attached 20% Divinylbenzene Polystyrene Analysis (c).

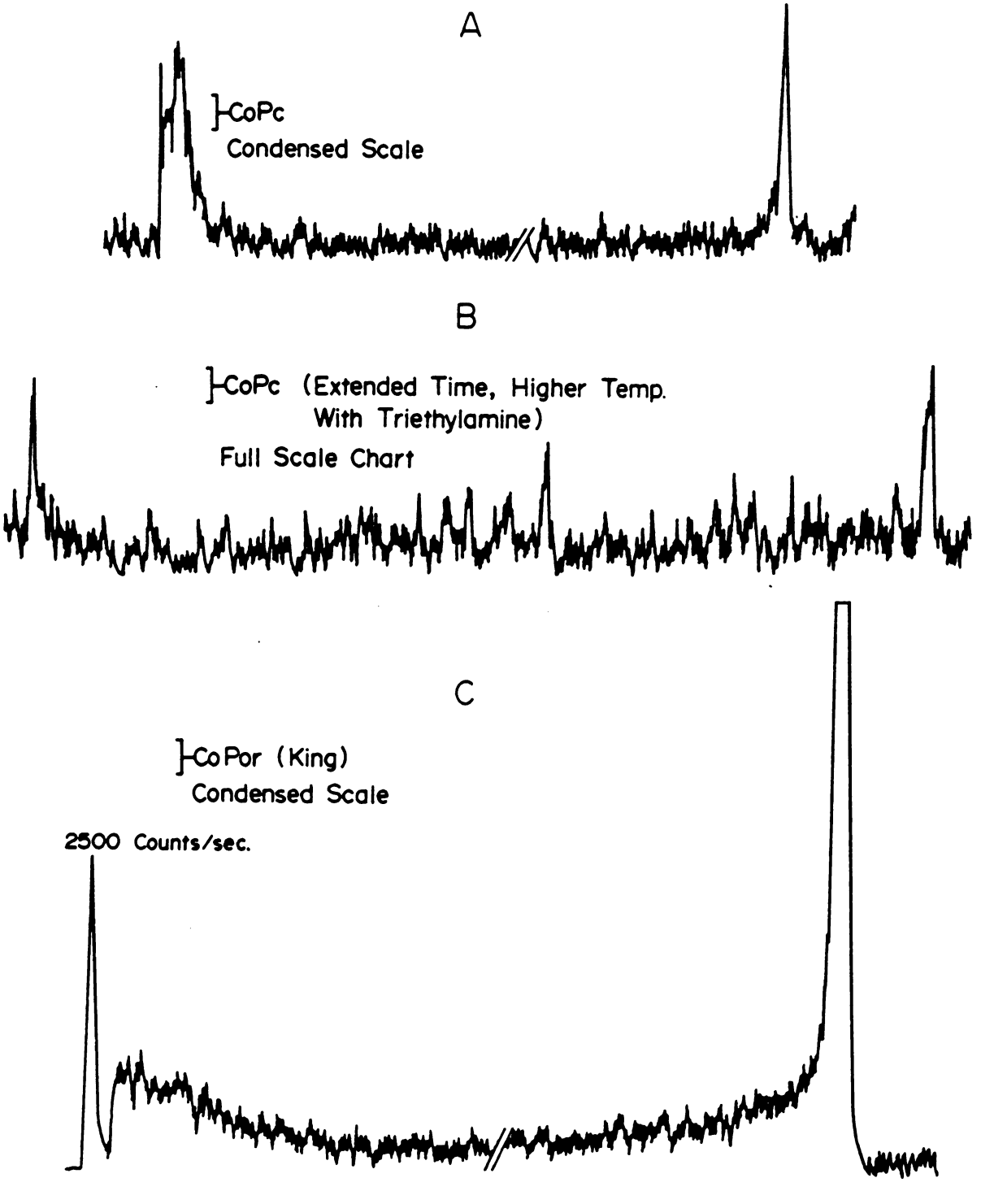

A
CoPc
Condensed Scale
B
CoPc (Extended Time, Higher Temp.
With Triethylamine)
Full Scale Chart
C
CoPor (King)
Condensed Scale
2500 Counts/sec.

Figure 8.

and the triethylamine results in some penetration to some interior sites but the distribution is far from uniform. There appear to be pockets in the interior of higher loading followed by rapid drop off of metal centers much as scanning across the surface boundry and then into the interior of a sample appears. Indeed, these pockets of high concentration of phthalocyanine approach the surface value of metal complex loading but sites surrounding the pockets are unreacted.

For comparison a sample was obtained of cobalt porphyrin attached to 20% divinylbenzene and a comparison SEM analysis carried out. This sample also displays the typical loading of the surface of the polymer bead but the interior of the bead remains unreacted. (See next chapter)

The SEM method was also used for elemental analysis since count rates at any particular point or an average count rate for a cross section can easily be compared to the count rate of the pure-metal, thus, a facile analysis results. This method proved consistantly more precise than trace elemental analysis by commerical atomic absorption. Results appear in Table I, p.18.

CHAPTER IV

RESULTS AND DISCUSSION

A. Result of Treatment of Metal Phthalocyanines with Chlorosulfonic Acid

In all, five different metal phthalocyanines were purchased along with metal free phthalocyanine for use in chlorosulfonic acid treatment steps so that $-SO_2-Cl$ groups would be attached to the aromatic, macrocyclic ring. As expected, only those compounds where the metal is tightly bound (Ni, VO) were able to withstand the highly acidic reaction conditions over a long period in which chlorosulfonic acid acted as reagent and solvent. Nickel phthalocyanine showed the greatest stability while vanadyl phthalocyanine showed marked resistance to attack by sulfuric acid in experiments designed to test their stability toward acid, Figure 9. However, iron phthalocyanine breaks down completely over a long reaction time in such a manner as to allow the acid to attack and degrade the macrocyclic ligand itself. Likewise, the macrocycle of metal free phthalocyanine visibly breaks down in acid as noted by the loss of its characteristically dark color. Experiments to show degradation as a function of time of the Co and Fe complex are displayed in Figure 10. For these compounds which are less

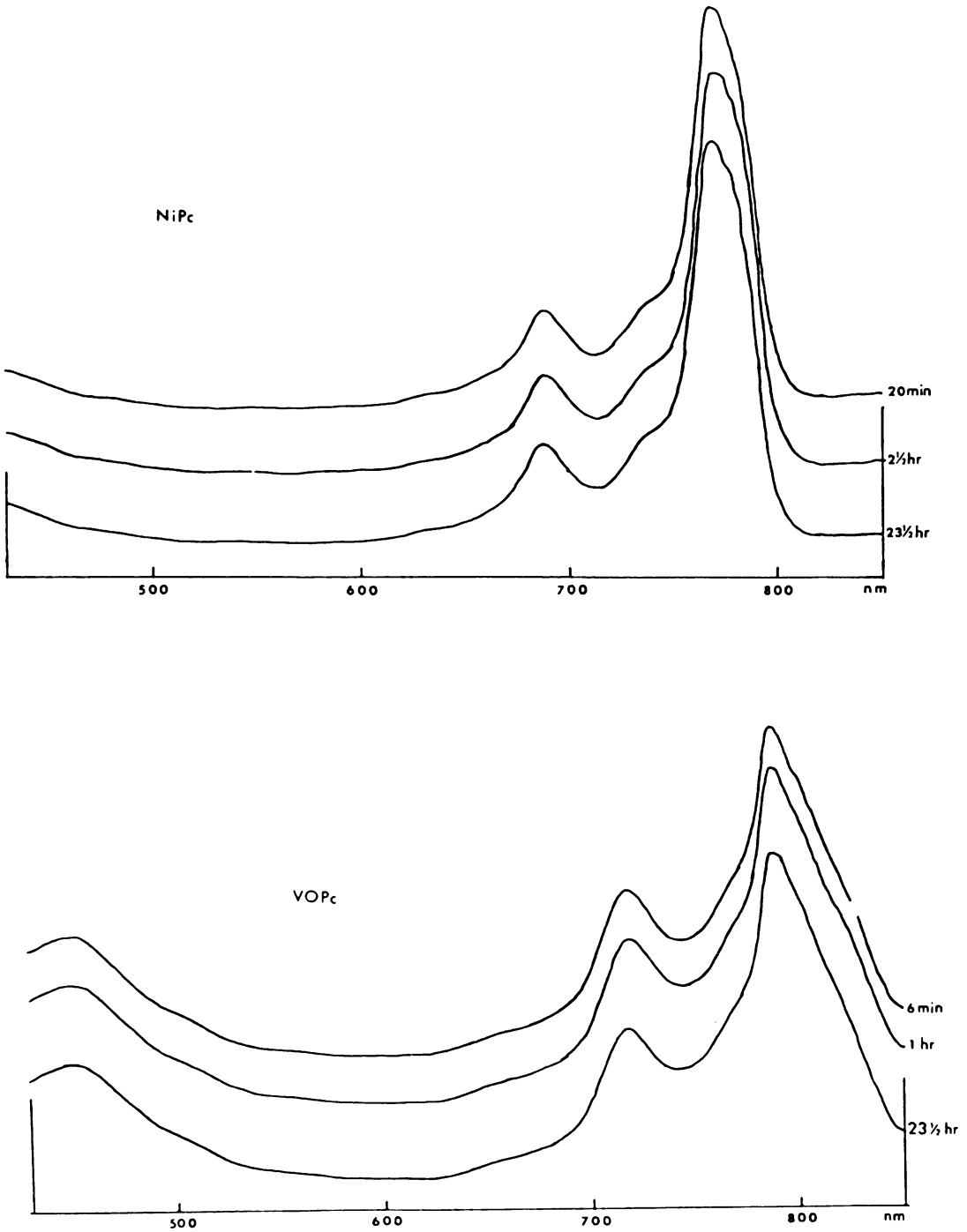


Figure 9. Visible Spectra of Nickel and Vanadyl Phthalocyanine in Concentrated Sulfuric Acid

stable in acid it is critical to adjust the reaction time so that enough of the macrocylic complex remains for subsequent reaction. That is, a competing reaction exists between chlorosulfonyl substitution and acid degradation of the complexes in question.

There are many factors that influence stability of particular phthalocyanine compounds[4], among which are covalent character, tendency toward square planner coordination, and ability of a particular metal to undergo oxidation state changes in the macrocyclic environment. Such factors coupled with the necessity of the highly acidic environment in the first step of both the sulfonylation and sulfonamide reaction sequence to produce the polymer supported metal phthalocyanines will, of course, provide a limiting condition which narrows the yield of the entire process. These phthalocyanines complexes with a marked degree of stability (Ni and VO) are favored over those which must be more carefully prepared (Co and Fe) and those which seem to produce no attached complex under controlled conditions (Mn and especially metal free phthalocyanine).

B. Results of Sulfonylation of Polystyrene - DVB Copolymer Beads with Metal Phthalocyanines

As mentioned in Chapter II, a sequence of reactions was undertaken at the onset of research into these supported phthalocyanine complexes to determine which reaction conditions would maximize the amount of metal complex loading. In addition, since the initial reaction to support nickel phthalocyanine on beads resulted in a product that contained beads of various hues, reaction conditions were sought that

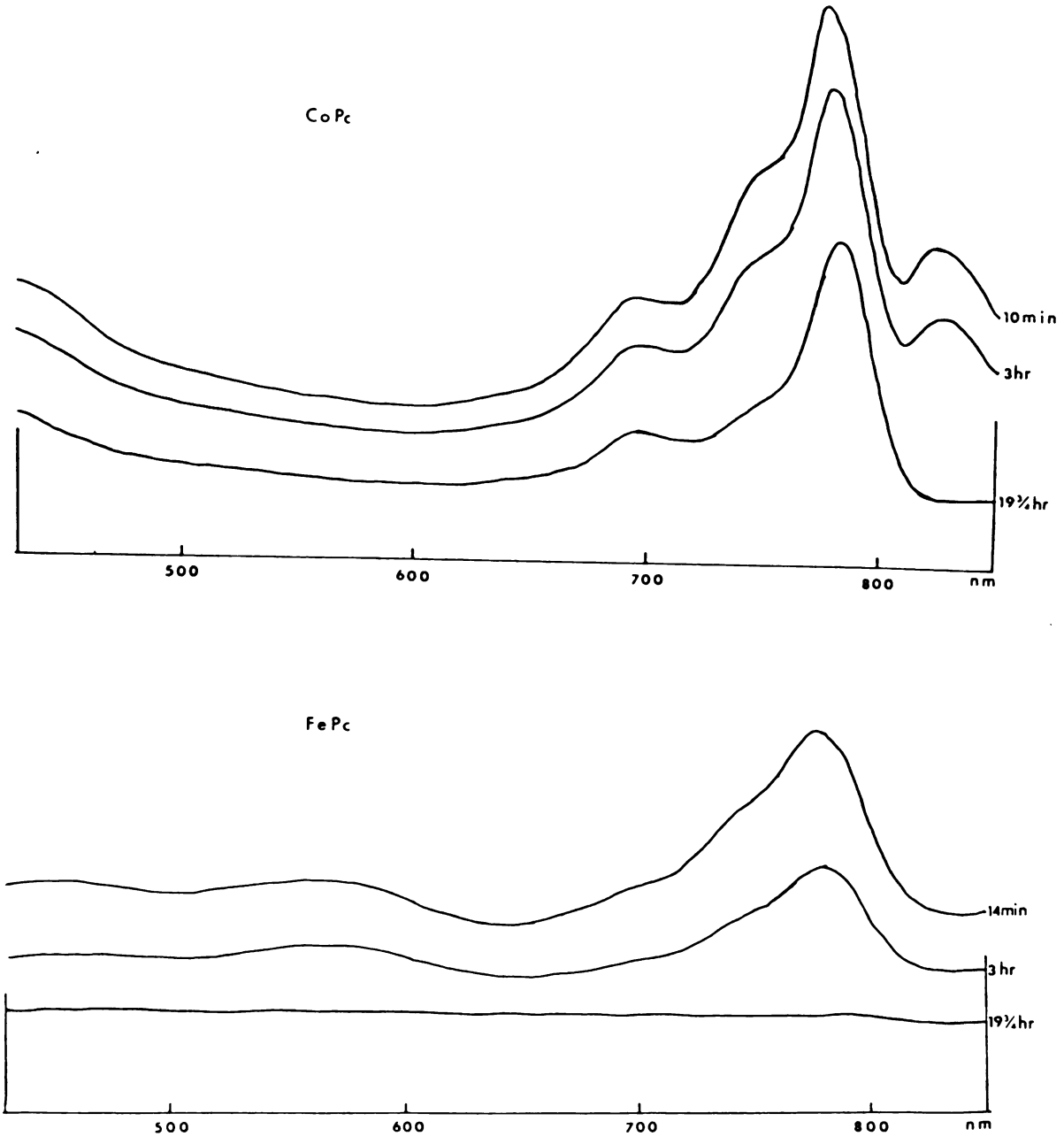


Figure 10. Visible Spectra of Iron and Cobalt Phthalocyanine in Concentrated Sulfuric Acid

would afford uniformly loaded beads.

The conditions adjusted in various reactions included time, temperature, amount of aluminum chloride catalyst, and sequence of addition of beads and catalyst to the reaction mixture; each will be considered in turn.

Time seems to determine the degree of loading up to a maximum, beyond which additional time does not effect total reaction. Therefore to insure that the time factor is overriden one need only to insure that sufficient time is allowed so that no further reaction takes place. Conversly if one wanted to lower the degree of loading the reaction time during the sulfonylation step could be shortened.

Temperature seems to effect both loading and homogeneity of color. Experiments were undertaken in the sulfonylation step at room temperature up to the reflux temperature of the solvent, nitromethane (101°C). Again it was found that loading could be increased to approximately 50-60°C. Above that temperature range it was apparent that loadings actually were lower. Such conditions might possibly be due to competition between the rates involved of the sulfonylation reaction at higher temperatures and exchange of reactant into and out of the pores of the beads. Indeed, such factors as exchange rate difference due to porosity difference from bead to bead would seem to account for the mottled apparance and, hence, the variable loading of the sulfonylation products. Another factor considered below is the denaturing of the beads by the aluminum chloride sulfonylation catalyst. Such effects are highly magnified at elevated temperatures.

The amount of aluminum chloride used as a sulfonylation catalyst

has two effects. The catalyst was always used in large excess of stoichiometrically required amounts, thus limitations by ordinary chemical factors were not considered, but in extremely large excess the beads seemed to denature and a brownish colored product was recovered from the reaction mixture. The other effect was mechanical. If too much aluminum chloride was added the resulting complex formed between it and the chlorosulfonated metal phthalocyanines turned into a thick, semi-solid mass which prevented stirring of the mixture. Additional solvent was required to relieve the situation and allow resumption of uniform stirring.

The sequence by which reactants were added to the reaction mixture seemed to have very little effect on the eventual outcome of the overall reaction. At first such considerations were made in an attempt to overcome the multi-shaded bead problem. Since the first sulfonylation did not allow sufficient time for the aluminum chloride to form a soluble complex with the chlorosulfonated metal phthalocyanine before the beads were added, initially it was thought that such a non-constant supply of reactant might be responsible for the non-uniform reaction on the beads. Subsequent experiments, however, showed very little difference in the final product from one experiment to another when the amount of time allowed for aluminum chloride-phthalocyanine intermediate complex formation was varied before addition of the polymer beads to the reaction.

Other factors that possibly might be considered to effect the degree of loading from bead to bead, such as stirring rate of the solution and mechanical trapping of the beads by precipitated aluminum

chloride-phthalocyanine complex, likewise, had a minimal effect on the outcome of the reaction sequence. Therefore, it seems plausible that the degree of difference in loading from bead to bead depends upon the ability of the pores of an individual bead to carry reactants into its available sites for reaction at any particular temperature.

C. Results of Sulfonamide Linkage Formation Between Polystyrene-DVB Copolymer Beads and Metal Phthalocyanines

This series of reactions was undertaken because of the problems encountered with sulfonylation reactions reported above. Additional steps were taken to purify the sulfonated phthalocyanines after the first step of the reaction and to neutralize any excess chlorosulfonic acid. That in addition to a shortened time in contact with chlorosulfonic acid during initial reaction allowed phthalocyanines of iron, cobalt, and manganese to be successfully used with polymer supports. It was not possible to prepare a metal free complex.

Also experiments were undertaken to check the effect of solvent on reaction outcome during the subsequent sulfonamide linkage formation. Again degree of loading and uniformity of loading was checked.

However, the sulfonamide formation reaction presented two additional problems which could not be solved.

The first was caused by the necessity to make amino substituted polymer beads. The procedure used nitric acid to nitrate the polymer and then the nitro groups were reduced with tin chloride to the amine. This step results in a formation of an apparent radical as is shown in

the ESR spectrum of the beads. These radicals might have been formed by incomplete reduction of the nitro groups to the amine as it is known that not all of the groups are reduced by the procedure.[22]

The second problem that arose during the procedure was a complete surprise. It had been known that the reactions with polymer supported phthalocyanines[5] and porphyrins[22] acting as catalysts seemed diffusion controlled. That is the reactions increased in activity when the beads were ground up. In fact just such a circumstance is shown with the reactions reported in the next section. However, since some members of this laboratory had investigated the interior loading of their beads by using scanning electron microprobe procedures, these compounds were also prepared for the procedure. Upon cutting the beads across its diameter it was clearly evident that the loading was not uniform. They showed a distinct coloration at the surface but virtually no color at the interior positions. Many experiments which involved changes of solvent, time and temperature showed little improvement in the situation. Since this loading problem created difficulty in interpretation of increase of activity with grinding the beads as pure diffusion control of the reaction, a sample of King's reaction product was obtained.[23] That sample also showed a marked difference upon sweeping the electron beam across its crossection in SEM analysis. The surface was 148 times more concentrated than the interior (Figure 8c). Thus, it is reasoned that the primary reaction takes place as the groups of reactants come into contact as chlorosulfonated metal phthalocyanines attach to active groups of aminopolystyrene on the polymer bead surface. Once attached these groups cause crosslinkage as

shown by DSC results in the previous chapter. In addition steric and electronic effects likely prevail and the result is a virtually closed surface which prevents any further reaction penetration. The result is for the surface to achieve a high degree of loading while the interior, even the near surface, is essentially unreacted. Experiments to block the surface or to increase penetration by mechanical effects were unsuccessful in greatly changing the overall effect. In some cases a "pocket effect" results, that is, an area of high phthalocyanine loading is surrounded by unreacted surface. One might speculate that these pockets are interstitial sites at channel openings at the surface or interior which become lined with phthalocyanine. In the extreme such loading could approach pure phthalocyanine content as, Dr. King's beads do at their surface. His relatively higher porphyrin to bead ratio at the surface compared to the phthalocyaine to bead ratio at the surface or at the "pockets" might well be attributed to the difference in internal structure shown between his bead and those reported here as shown by their electron micrograph. His are more highly packed in internal structure.

If, in fact, loadings approach values of pure phthalocyanine or porphyrin crystals it is necessary to conclude that site isolation does not occur and that catalytic behavior of the supported complexes cannot be expected to be much higher than that of unreacted phthalocyanine. Further, increase of reaction toward oxidations after bead grinding, classically attributed to diffusion control, is most likely just a mechanical effect whereby more active centers are exposed to substrate, much as grinding crystals of unsupported material would increase

activity of the compound.

D. Result of Oxygen Uptake Studies

The oxygen supply manifold showed some difficulty in use especially in those reactions which resulted in very low uptake of oxygen. It became apparent that the air flow about the manifold could affect the readings of gas uptake by as much as plus or minus 5 mL. One had to be certain that the laboratory remained opened or closed to insure a constant degree of room air exchange throughout the time readings were taken. The mercury manometer proved to be inconvenient to use in measuring the amount of oxygen loss to the chemical system. That task was greatly simplified by maintenance of ambient pressure by adjusting the leveling bulb of the gas buret such that a constant pressure was held in the gas manifold as shown by the oil level in the oil bubbler overpressure device.

The chemical systems tested also exhibited certain patterns. For instance, those which were only slowly oxidized did not take up oxygen quickly enough for the data to show any variation other than random pressure increases or decreases ascribable to external factors such as changes of temperature and air pressure. For those systems in which significant oxidation took place there was a usual incubation period of about two hours during which the rate of oxygen uptake increased to a constant value. Such behavior can be attributed to the necessity of the solvent/reactant to establish equilibrum with the active catalytic centers and, hence, the time lag necessary for the metal centers to

form an available dioxygen complex intermediate. In some reactions the beads were recovered, washed and dried then immediately reused in a second run. The results were displayed as time vs uptake of oxygen for nickel phthalocyanine complex, Figure 11, and iron phthalocyanine complex, Figure 12. These are typical of the reactive systems. Other graphs are found in Appendix B. Each of these systems, the nickel phthalocyanine complex made by sulfonylate linkage and the iron phthalocyanine complex made by sulfonamide linkage, were used as oxidation catalysts toward cyclohexene which was acting as both substrate and solvent for the systems. These data along with those for the other complexes tested (graphs in Appendix B) are summarized in Table II which also includes data for the oxygen uptake of the standard, non-attached, phthalocyanines. Comparison of rates of uptake for attached phthalocyanine vs unattached compounds can be found in the following section, however, a few comments and conclusions can be drawn from the inspection of the data for attached phthalocyanines.

First, note that in all cases the incubation time is approximately two hours, followed by a period of uptake of oxygen which is nearly linear. The period lasts for two to two and one-half hours in which the amount of oxygen uptake increases. Such behavior can be attributed to two competing factors. One is the necessity to form the metal dioxygen intermediate before further reaction with substrate. The second is, of course, the actual oxidation of the organic substrate. Both reactions utilize available oxygen with a corresponding lowering of the gas presure in the supply manifold. Non linearity can be caused by lack of equilibrium between the formation of the dioxygen

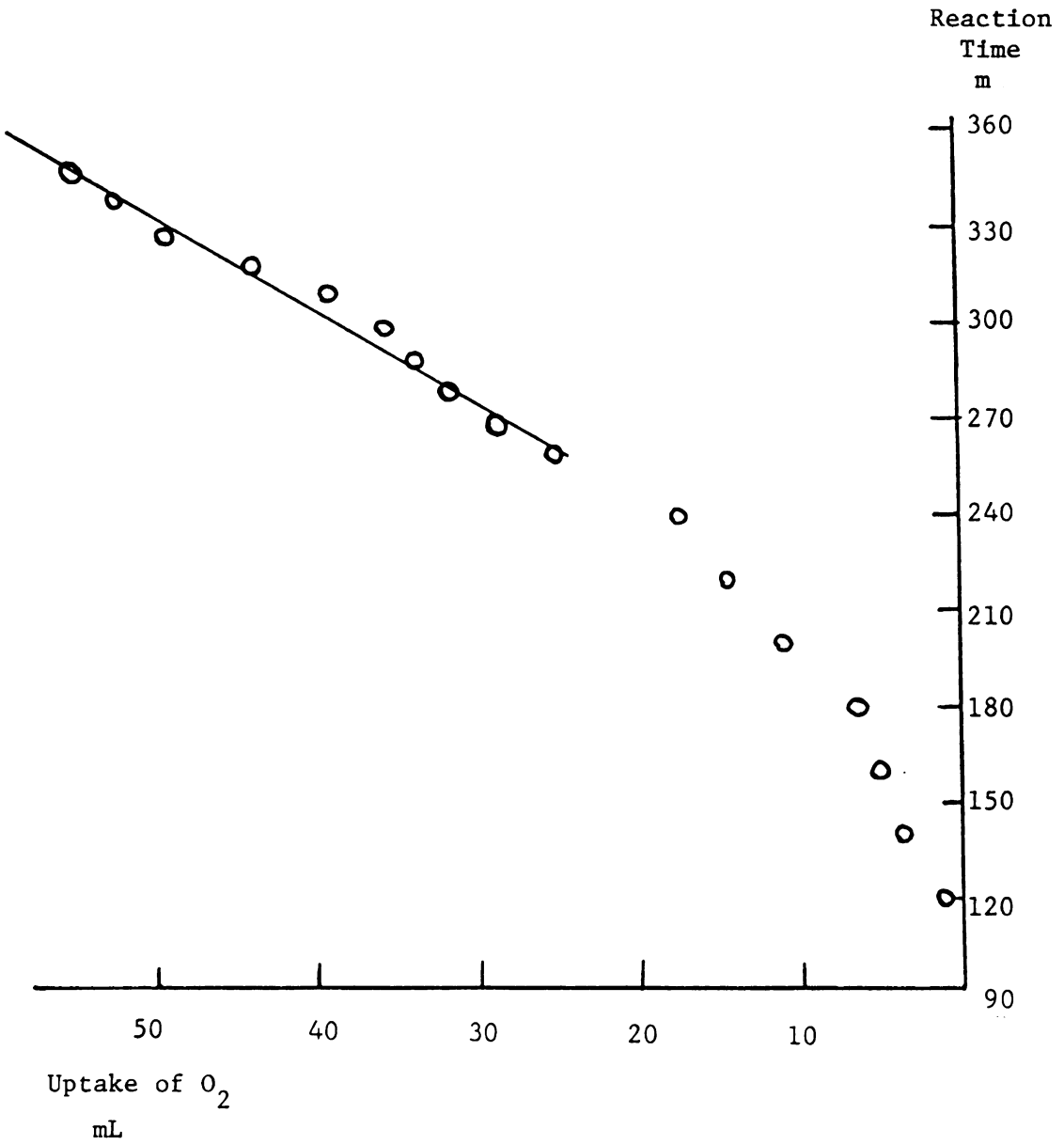


Figure 11. Polymer Supported NiPc (new) In Oxidation of Cyclohexene at 78° C

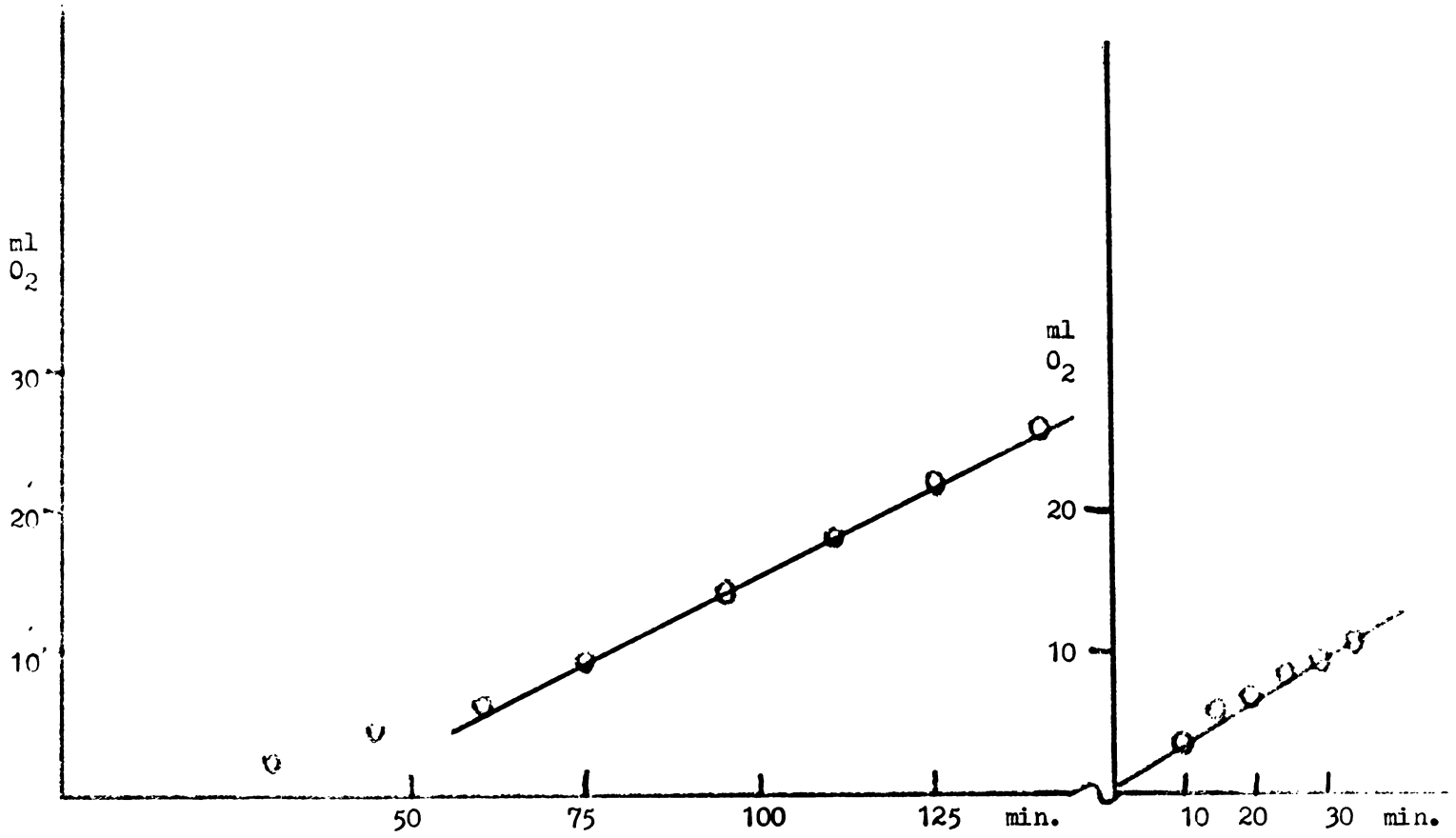


Figure 12. Polymer Supported FePc (new) In Oxidation of Cyclohexene at 78°C.

TABLE II. Rate of Oxygen Uptake for Phthalocyanine Catalyzed Cyclohexene Oxidations (78°C)
(20% DVB-Polystyrene Beads)
(0.1 g Beads, 3mL Cyclohexene)

Table II

Catalyst	Measured Rate (mL O_2/m)	(mL O_2/m/mmole-Metal)
Supported NiPc (Sulfone) (New)	0.34	1814.7
Supported VOPc (Sulfone) (New)	0.42	7924.1
Supported NiPc (Sulfone) (Used)	0.26	1387.7
Supported VOPc (Sulfone) (Used)	0.37	6980.7
Supported NiPc (Sulfone) (Ground)	0.37	1974.8
Supported CoPc (Sulfonamide) (New)	0.29	712.1
Supported FePc (Sulfonamide) (New)	0.25	377.3
Supported MnPc (Sulfonamide) (New)	0.15	-----
*NiPc $(SO_3Na)_4$ Standard	0.42 (day 1)	2900.97
*NiPc $(SO_3Na)_4$ Standard	0.26 (day 2)	1795.8
*NiPc $(SO_3Na)_4$ Standard	0.16 (day 3)	1105.1

*The same reaction monitored over parts of 3 days.

intermediate-substrate intermediate and its subsequent breakup to the final oxidation products.

Comparison of the "new" polymer supported catalysts, those which had not previously been used in a reaction; with beads which were termed "used" because they had been recovered from one reaction mixture and used again, shows that in each case a small amount of reduction in overall oxygen uptake rate occurs. Such a reduction is usually considered to be caused by poisoning of the catalytic centers. Neither used nickel beads nor used vanadyl beads display deviation from linearity over the portion of the reaction monitored (even though the reaction was allowed to incubate overnight) argues that substantial poisoning of catalytic activity does not take place. Such changes in overall rate might well be assigned to shifts in equilibrium in the reaction mixture due to the buildup or breakdown of the substrate and its oxidation products. Finally, the comparison of values in Table II show that the reaction rates of ground nickel complex beads is slightly higher than the oxygen uptake rate for the whole beads of the same compound. As detailed earlier, the apparent increase in rate for the ground beads is most likely due to the mechanical separation and, hence, availability of a greater amount of active centers rather than strict diffusion control of the reaction.

E. Result of Oxidation Studies Measured as Total Percentage of Substrate Conversion

As early as 1939 Paquot[24] had documented the oxidation of cyclohexene with phthalocyanines acting as catalysts by measuring total conversion of substrate into oxidation products. He reported yields of 3-cyclohexen-1-one, 3-cyclohexene-1-ol, 1,3-cyclohexadiene, epoxycyclohexane, and 1,1-cyclohexanediol. Of course, at that time he did not have instrumental means of analysis and relied upon chemical means for separation and identification of the products. With the exception of the 1,3-cyclohexadiene, gas chromatographic data shows that, indeed, these are the products formed of the reactions reported here. The 10% SE-30 column used for the separations was standardized against authentic samples of each of the possible oxidation products and showed good resolution of all but the diene which proved to be nearly coincident in retention time to the parent cyclohexene. However, by adjusting the chromatograph's flow rate and temperature it was found that the two substances would be separated. Some loss of peak resolution did, however, result. Therefore, while the presence of the diene is not ruled out, the shape of the parent peak in a chromatogram run at normal temperature (100°C) and the absence of anomalies in the chromatogram when standards are run at lower temperatures indicate that very little or no diene is present in the reaction mixtures under question here.

The gas chromatographic data for the various polymer supported

complexes are given in Table III. All reactions except for the one for the sulfonated standard nickel phthalocyanine were run on a simplified oxygen manifold described in a previous chapter. All reactions were 47 h in duration.

A number of trends can be seen in the data. First the systems show a dependence on reaction temperature. Nickel and vanadyl complexes display little oxidative activity toward cyclohexene below 78°C. That temperature was chosen because the boiling point of cyclohexene is very close at 83°C. The dramatic increase in overall conversion of cyclohexene into oxidation products at higher temperatures is most likely due to the activation energy, and possibly increased penetration of the reactant/solvent into a few layers of the polymer bead matrix. Also of note is that, although little product is actually formed, there seems to be a preference for the formation of 1, 2-cyclohexandiol as is seen by the small concentration of that particular product in reactions run at 53°C. At higher temperatures other reaction products begin to form. In 1939 Paquot attributed their formation to two modes of oxidative action. One was direct metal-oxygen attack on the double bond of cyclohexene; attack which results in epoxyhexane and the 1,2 cyclohexandiol. The other mode of oxidation was attributed to attack of the double bond which was claimed to cause formation of 3-cyclohexen-1-one and the 3-cyclohexene-1-ol.

Although the actual mode of oxygen attachment to metal complexes in large macrocyclic ligand systems is still a matter of much controversy,[25] current work, which has primarily centered around biological dioxygenases, has suggested possible modes of reaction in

Table III. Oxidation Product Conversions of Cyclohexene Catalyzed by Bound Phthalocyanine Complexes.

Table III

Compound (All are 20% DVB polystyrene beads)	Temperature °C	Cyclohexene unconverted %	Epoxycyclohexane %	3-Cyclohexene-1-ol %	3-Cyclohexene-1-one %	1,2-Cyclohexandiol %	Others
1. Supported NiPc (1.87×10^{-4} mmole)	26	100	---	---	---	---	---
2. Supported NiPC (1.87×10^{-4} mmole reaction)	53	94.1	Trace	Trace	Trace	5.9	---
3. Supported NiPc (1.87×10^{-4} mmole reaction)	78	44.4	0.8	18.99	26.4	9.4	---
4. Supported NiPc (1.87×10^{-4} mmole reaction) (ground)	78	13.9	3.3	30	33.7	19	---
5. Supported VOPc (9.30×10^{-5} mmole)	26	100	---	---	---	---	---
6. Supported VOPc (9.30×10^{-5} mmole reaction)	53	99.4	---	---	---	0.6	---
7. Supported VOPc (9.30×10^{-5} mmole reaction)	78	47.8	0.9	18.3	31.5	0.8	0.7
8. Supported VOPc (9.30×10^{-5} mmole reaction) (ground)	53	97.9	---	---	---	2.1	---
9. Blank With Plain Beads	83	86.9	0.5	6.5	3.6	2.5	---
10. Blank Cyclohexene	78	77.3	2.3	7.8	5.9	6.7	---
11. Standard NiPc (1.45×10^{-4} mmole reaction) (SO_3Na_4)	78	36.8	3	16.9	22.2	21.1	---

such systems. For instance, it is known that O_2 will not add directly to C=C. [26] However, if O_2 binds to a transition metal complex and forms a superoxide in which there is not much backbonding, the superoxide should behave as though it were a free radical. It is proposed that tryptophan dioxygyenase and metapyrocatechase act in such a manner, Figure 13. If the double bond is in a cyclohexene ring, subsequent breakdown of the strained four membered ring by proton abstraction would result in production of the diol product. Also arguing strongly for the formation of the superoxide is that its formation has been proposed for the formation of dioxygen bridged dimers in cobalt systems, [27] which would be similar to those proposed for certain (Fe,Co,Mn) phthalocyanines, Figure 2. Likewise, monooxygenase biologic systems are known[24] in which a superoxide metal complex picks up an electron to form the peroxide, which can react with a double bond to form an epoxide. Furthermore, such biologic systems are known to insert oxygen in carbon hydrogen bonds to form alcohols. If such attack were directed to the α position of a cyclohexene double bond the resulting product would be a hexenol and hexenone.

While such arguments are reasonable to explain the product formations especially for those complexes in which the electronic potentials favor stable peroxide attachment namely iron, cobalt, and managanese, the proposed lack of site isolation favors dimer formation between phthalocyanine rings which at least partly removes the oxygen from availability for oxidative attack on the substrate.

It is particularly noteworthy that the other complexes which

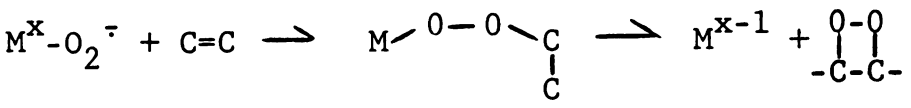


Figure 13. Superoxide Attack of Double Bond.

about the same reactivity in terms of oxygen uptake as the others (Fe,Co,Mn). In fact by checking the uptake per amount of catalyst column of Table II it might be suggested that nickel and vanadyl complexes are more reactive than the iron, cobalt, and manganese counterparts. Since these are the compounds which are least likely to form complexes which mimic biologic counterparts it is evident that other oxidative pathways are available to the system. The lower activity of the other three complexes is, however, another point of evidence which suggests a high degree of loading is occuring in spots because just such a condition would result in dimer formation and loss of further reactivity. These total conversions over a two-day period show overall more activity of the systems which include the polymer supported metal complexes over blank solutions, or blank solutions with just plain polymer beads. Total conversion is 22.7% on blank cyclohexene undergoing autoxidation compared to 86.1% conversion for the most reactive complex-substrate experiment undertaken under the same reaction conditions. One final note is that the beads themselves seem to reduce the reaction rate, as is seen by comparison of the two blank solutions in Table III. Pure cyclohexene undergoes autoxidation to the extent of 22.7% vs 13.1% conversion of the cyclohexene with plain beads. The lowered reactivity is most likely due to the interference with any free radical mechanisms by the polymer beads.

F. Non Attached Phthalocyanines Standard Results

These data are shown in Figure 14. Both the oxygen uptake and

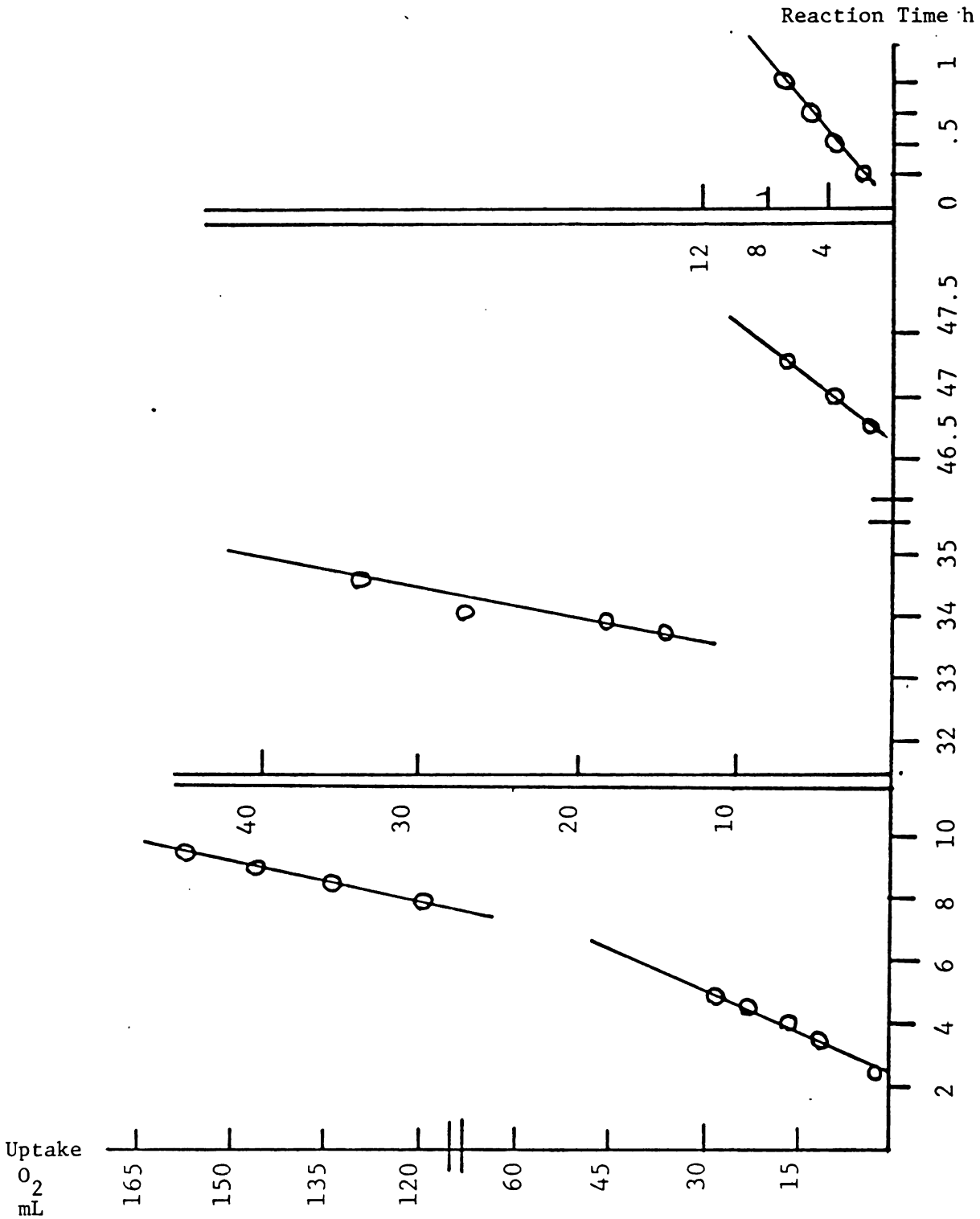


Figure 14. Standard NiPc-tetra sodium sulfate in oxidation of Cyclohexene at 78°C.

final percentage of conversion of substrate into products were measured. As expected the rate of the reaction drops substantially as the reaction proceeds due to shift of equilibrium as product/reactant concentration changes. The reaction rates, themselves, measured over the course of the reaction show a markedly similar value to those of the supported nickel beads both "new" and used for one day. Comparison of total conversion data show, again, the similarity between attached nickel complex and its corresponding unattached standard.

Comparison of data for the ground nickel beads to the standard-unbound nickel phthalocyanine suggests that enhancement of rate appears to take place. This enhancement, while not great, is probably due to particle size of the ground bead and so actual availablity of metal centers.

G. Other Experiments Carried Out Toward Oxidation with Supported Phthalocyanines

In addition to the oxidation of cyclohexene attempts were made to test cumene, toluene, and both 1- and 2-octene as reactive substrates. Very small amounts of oxidation products were found by gas chromatographic analysis for the octenes but in such small quantity that they could not be measured by the instrument's integrator. No products were found for cumene and toluene although the oxidation of cumene and toluene are known to be catalyzed by phthalocyanine systems.[26] Such low reactivity was at first thought to be caused by the inability of the substrates to swell the polymer matrix and penetrate to active centers even though toluene should easily penetrate

polystyrene. In fact experiments were designed in which 1,2-dichloroethane was added as a swelling agent to the usual reaction solvent of cyclohexene. (Graph in Appendix B). The addition of the solvent was seen to hamper the reaction possibly by simple competition at the bead surface for the reactive sites available by a concentration effect or possibly by solvent reaction with any free radical formed. This latter possibly seemed unlikely, since no extraneous peaks were seen upon GC analysis. One further possibility is that swelling of the bead may be selective such that the chlorinated solvent penetrates the bead leaving the cyclohexene in higher concentration in the bulk solvent.

For solvents which otherwise would swell the bead but do not oxidize under these conditions (toluene), steric restraint as they approach the active metal centers on the surface could account for the limit on overall production of products.

CHAPTER V

CONCLUSIONS

Clearly the usefulness of a hybrid phase catalyst rests upon the environment in which the active catalytic metal center are placed. The environment is caused by the support to which the active complex is attached and its ability to modify the electronic nature of the catalytic metal centers as well as its mechanical limitation of the approach of substrate to the centers.

These experiments were carried out with the use of commerically available polystyrene resins which are normally used in the manufacture of ion exchange resins. As such their physical characterists are designed to allow penetration of small ions to active centers located within the beads of polymers. In fact it is the channel size (displayed in the electron micrographs) which made these supports initally interesting. Support of catalytic centers by Zwart[5] and Rollman[15] had been carried out with varying degrees of success when the resulting hybrid phase complexes were used as catalysts. Zwart had used a long side chain linkage to support his complexes thereby increasing the effective diameter of the catalytic species which was subsequently reacted with polystyrene. He then reported negligible

increase in results when the supported complex was used in oxidation reactions. He attributes the low reactivity to non penetration of substrate into the polystyrene matrix.

Likewise, many studies have concluded that site isolation was necessary to increase catalytic activity of individual metal centers.[5,22] The use of a supporting medium for the catalysts provided a means to mechanically separate the centers with resulting increases in activity displayed when these hybrid complexes were allowed to react as catalysts. The experiments carried out here were made with an attempt to maximize the desired effects, that is to allow separated metal centers to react with easily accessible substrate to provide effective, inexpensive catalysts for oxidation reactions. Thus, the sulfone and sulfonamide linkages utilized resulted in short side chains on the phthalocyanine moiety with supposed better penetration of the catalyst centers into the polystyrene during production of the supported complex and suggested greater allowance of penetration by substrate materials in subsequent reactions. Toward site isolation many different reaction conditions were carried out while producing the supported complexes to attempt to spread out the distribution of the active centers. These conditions included variance of time, temperature, and amount of reagents; and the use of blocking agents and chemical "scavengers" to pickup by products of reactions. The latter two methods provided a better distribution of centers, however, since site isolation did not appear to take place (See below).

Interestingly, at this time, the study of S. Stinson, suggests that research on polymer bound catalysts in general has reached a

standstill due to lack of information on the physical character of the catalyst attached compounds.[28] Indeed, the study which was carried out with ESR, DSC, SEM, and electron microscopy resulted from the need for knowledge of the character of the attached complexes.

Thus, using the theories of site isolation and mechanical blockage as starting points the data clearly indicates the nature of the environment around the polystyrene attached metal phthalocyanines. While the hybrid phase complex is forming it is apparent that site isolation does not occur. This is especially notable in the sample sent to us by Dr. King in which the level of metal complex at the surface of the polymer bead is essentially that of a pure crystal of the unattached metal complex. The point by point analysis of the compounds by SEM allows the conclusion that at the surface and in "pockets" in the interior the buildup of metal centers is very great, therefore, the desired site isolation with distribution of the catalyst does not occur to a large extent.

Likewise, the groups of catalysts in one area of the bead especially at the surface allows a physical change in the catalyst itself. The electron micrographs and DSC data attest to the change in character as do macroscopic observations such as mechanical splitting of the bead. The DSC shows that the exothermic changes in the bead result from treatment of the polystyrene with phthalocyanines. However, the micrographs are particularly striking showing that the surface is virtually closed and that, while the interior of the polymer beads is open, the surface is closed to substrate penetration. Thus, the data suggests that phthalocyanines do not isolate themselves with

attachment to polystyrene by these methods. The physical character of the reacted polymer is such that it results in the closing of the interior of the bead to substrate penetration. Both of these factors explain the only moderate rates of oxidation displayed in subsequent reactions. It can be concluded that neither the phthalocyanine or the polystyrene backbone are responsible for the limitation of oxidative ability but rather the reaction method necessary to place the two components together. Ordinary chemical methods to enhance the desired result of site isolation proved ineffective and suggests that a polymer would have to be designed in which the phthalocyanine moiety is incorporated into specific sites in the monomer before the formation of the metal complex containing polymer to achieve site isolation.

PART II

CHAPTER I

INTRODUCTION AND EXPERIMENTAL

INTRODUCTION

In continuation of electron transfer reaction studies in transition metal organometallic compounds made recently by this research group[29-30] the possible modes and kinetics of the electron transfer between titanocene dichloride (biscyclopentadienyl titanium dichloride) and its reported reduction products[31-33] were investigated. Since the titanium (III) contained in the reduced complexes gave a strong signal in electron spin resonance spectra of these compounds, the degree to which the electron spin linewidth broadened as various amounts of the unreduced titanocene dichloride was added to the system provides the probe to determine the rate of electron transfer. Both chemical and electrochemical methods were used in attempts to produce the reduced titanium containing complexes.

EXPERIMENTAL

1. General

The titanocene dichloride was purchased from the Alfa Chemical Company, Lot 080880. All studies were carried out in tetrahydrofuran (THF) which had been distilled under argon and over sodium. Solutions were prepared in a dry box under nitrogen. Syringes were used for both transfer of solutions and measurement of solution components. ESR tubes were filled in the inert atmosphere dry box, capped with a rubber septum, and immediately sealed with an oxygen/gas torch upon removal from the port of the dry box.

2. Electrochemical Reduction of Titanocene Dichloride

Since it has recently been reported that titanocene dichloride is reduced electrochemically to $[Cp_2TiCl_2]^-$ in THF[31], the original conditions in an attempt to produce a reduced titanium complex from titanocene dichloride utilized an electrochemical cell with a mercury working electrode with a saturated calomel electrode as a reference. Power was supplied by a PAR Model 174 cyclic voltammetry device set at constant potential. Although the characteristic dark red color of the 0.05M titanocene dichloride changed to a light yellow-orange under applied voltage no ESR signal was displayed from the reacted solutions. Cyclic voltammagrams were taken, Figure 15, which suggest the process is not cleanly reversible; see Discussion Section.

3. Reduction of Titanocene Dichloride by Chemcial Means

Hydrogen, zinc, and aluminum activated with mercury and aluminum

Figure 15. Cyclic Voltammogram of Titanocene Dichloride in THF (0.05M).

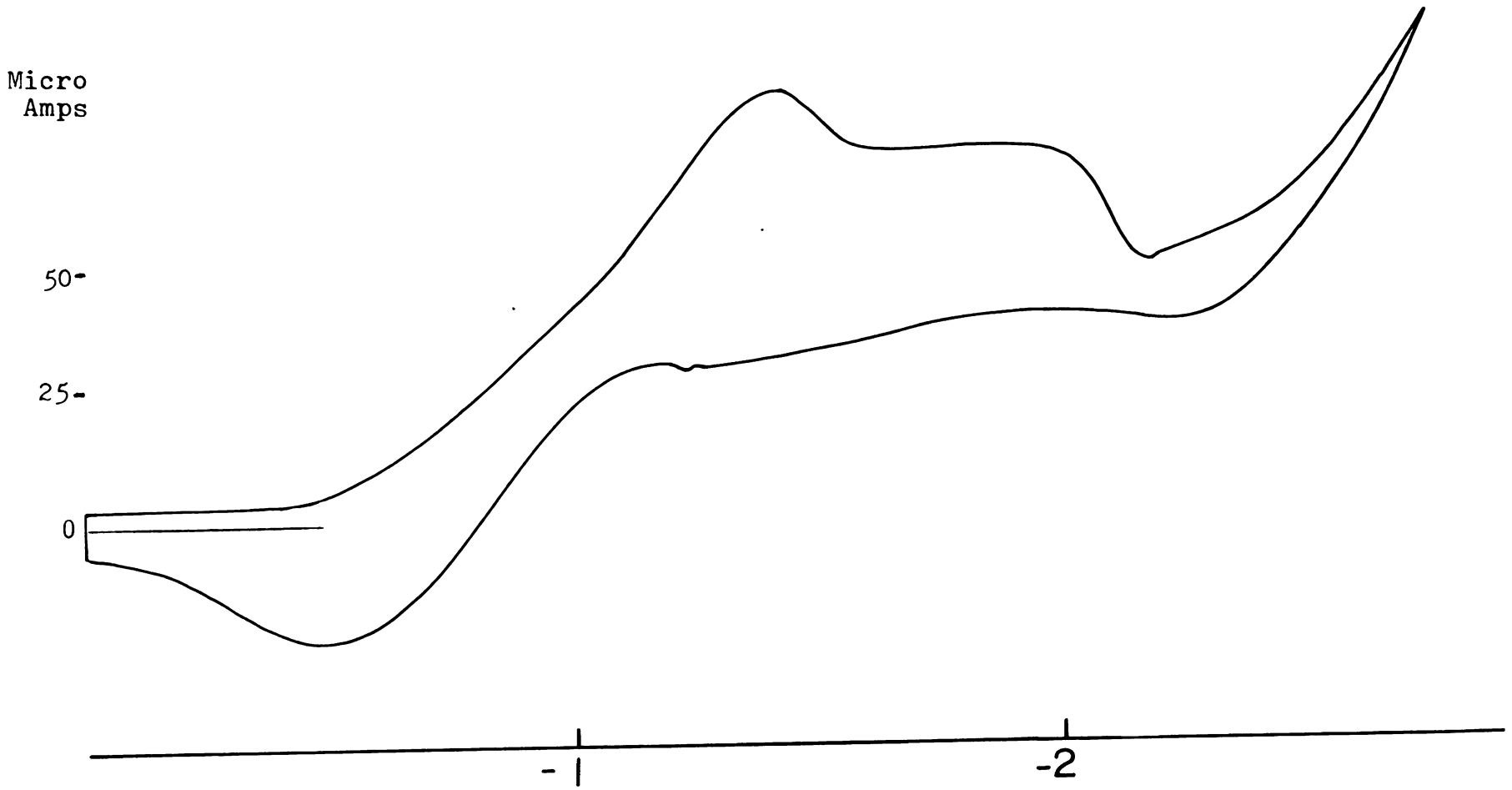


Figure 15.

by itself were tested as possible reducing agents toward titanocene dichloride. In the cases of hydrogen and aluminum attempts were made to treat the reducing mixtures with HCl gas to preclude the formation of dimerized product by loss of chloride from the complexes. All reductions were carried out in THF prepared as above to give approximately 0.05M solutions of titanocene dichloride. In the cases of hydrogen and aluminum with HCl gas no reaction was evident. With zinc there appeared to be a near immediate reaction when the solution was shaken under inert atmosphere with zinc dust (total reaction time less than 15 min.). When filtered the solution produced an ESR signal which persisted for several hours. If shaken for longer periods the red-orange solution produced from immediate reaction with zinc turned more greenish in color. While the solution treated with zinc for these longer periods had an ESR signal it was somewhat diminished in intensity to those signals of the solution treated with zinc for a shorter period of time.

Both aluminum powder and aluminum foil were used as reducing agents; however, the aluminum foil was first "activated" after the method of Coutts, Wailes, and Martin.[32] Small squares (about 1 cm^2) were treated with hot deoxygenated mercurous nitrate solution in water. After 30-60 seconds the water was poured off under argon and THF was introduced to the flask several times to wash the foil. The aluminum so produced was used in experiments with titanocene dichloride straight, with addition of HCl, and with addition of tetrabutylammonium chloride. All reductions were carried out under inert atmospheres.

4. Mixtures of Titanocene Dichloride and Reduced Titanocene

Dichloride Complexes

These mixtures were prepared in the dry box in volumetric flasks by using reduced compounds with displayed ESR and the "parent" solutions of titanocene dichloride which had been diluted from the approximately 0.05M concentration to various values down to 10^{-4}M. Colors varied from a dark red to a very light pink before addition of reduced components. While the amount of reduced complex varied from one sequence of experiments to another, its concentration within a specific reaction run to measure ESR linewidth was kept constant so that the effect on the spectra would be due to concentration of the parent compound alone.

5. Electron Spin Resonance Spectroscopy and Analysis of Reduced Products

All ESR spectra were taken on a Varian Model E-4 Spectrometer. Analyses of the reduced products were made by mass spectrometry and commerical elemental analysis.

CHAPTER II

RESULTS AND DISCUSSION

1. Electrochemical

Although the solutions changed color to give a light yellow green solution which would suggest that the titanocene dichloride was reacting, the solutions so formed displayed no ESR signal and had a cyclic voltammagram different from those literature reported analyses for $[Cp_2TiCl_2]^-$ [31] In addition the yellowish solutions were stable in air and did not go back to their original red color after exposure to oxygen containing atmosphere. These condiions suggest that -OH or -O- groups have replaced chloride in the titanocene dichloride and, thus, water vapor or oxygen is incorporated in the electrochemical cell as the reducing process is attempted.

It is important to note that, while in the specific cell used a positive pressure of argon blanketed the solution, it was open to the atmosphere at the top. Murr[31] claims his cells were "high vacuum" design which resulted in consistent voltammagrams. In addition the presence of the electric potential might have hastened the abstraction of oxygen from the solvent THF by the titanium complexes in solution.

2. Zinc Reduction Reactions

The use of zinc readily produced a complex which contains titanium (III) and has a strong ESR signal. Published reports attribute the signal to a titanocene monochloride but in the presence of a bimetallic complex of titanocene dichloride and zinc, $(Cp_2TiCl_2)_2Zn$ formed.[32] These solutions remain stable for periods of hours if care is taken to exclude air from the system. It is reported[32] that the bimetallic complex limits the amount of reduced titanium (III) produced by chemical competition. ESR data are reproduced in Figure 16 at both room temperature and 77K. These spectra bear strong resemblence to those reported very recently for a reduced titanocene chloride complex produced by gamma radiation which is attributed to reduced titanocene dichloride anion[33] but the author does not completely rule out the possible presence of titanocene monochloride.

Use of the reduced complex to make solutions with parent titanocene dichloride and the ESR spectra were very disappointing because the introduction of even very low concentrations of the parent resulted in complete loss of signal. The causes of the loss of the signal include the probable very low concentration of reduced complex owing to the formation of the bimetallic complex or a chemical transfer reaction between parent and bimetallic complex or between reduced complex and parent but on a very fast time scale. The latter cause seems unlikely in view of the results with the aluminum reduction (see below) which results in apparent electron transfer between parent and reduced titanium (III) complexes which are of similar nature to those proposed (titanoxene monochloride, or reduced titanium dichloride anion) for reduction with zinc. The presence of a complex of a higher molecular

Figure 16. ESR of Zinc reduced solutions of Titanocene Dichloride in THF (0.05M).

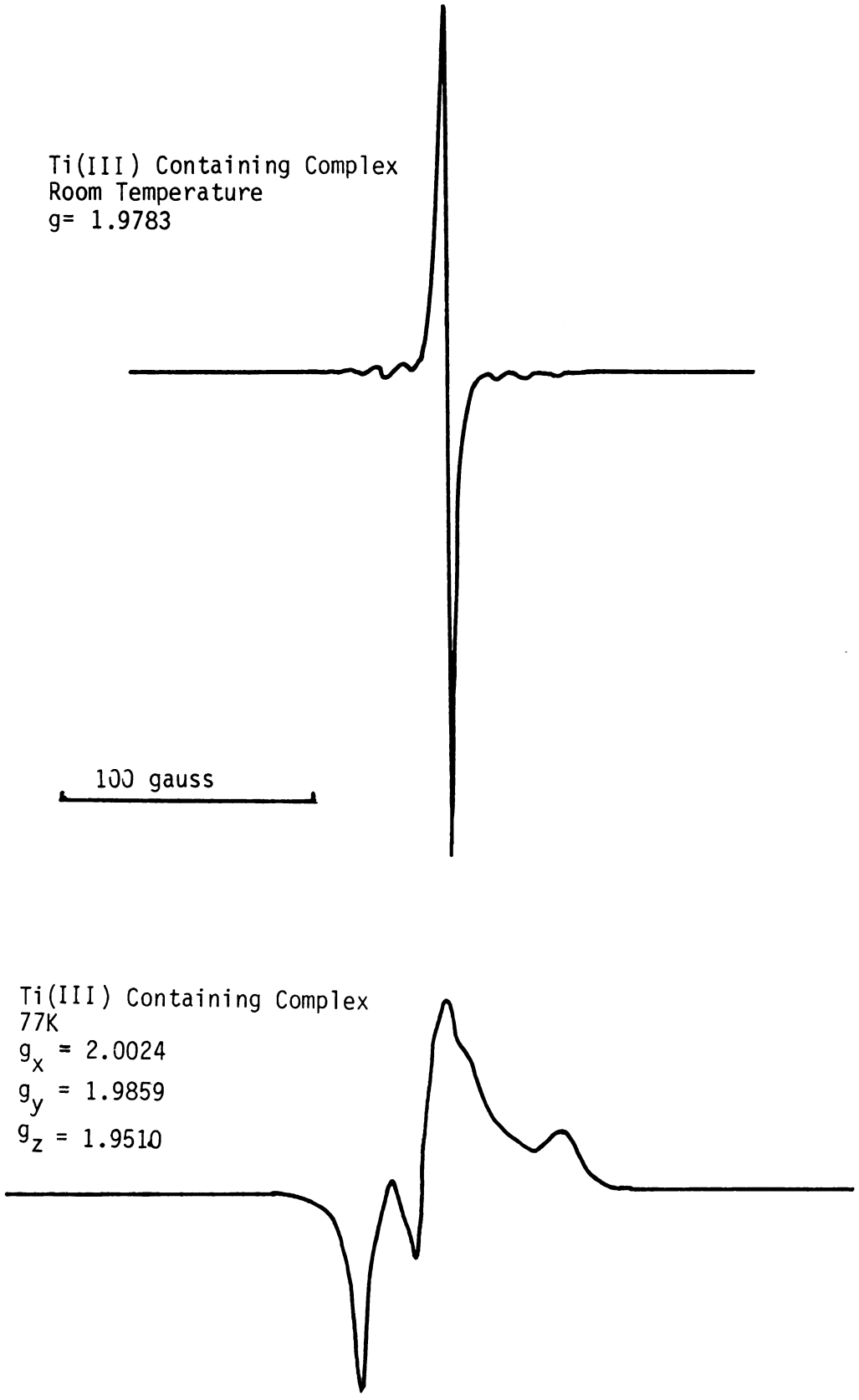

Ti(III) Containing Complex
Room Temperature
g= 1.9783
100 gauss
Ti(III) Containing Complex
77K
g_x = 2.0024
g_y = 1.9859
g_z = 1.9510

Figure 16.

weight than the parent titanocene dichloride is confirmed by mass spectrometry, Figure 17.

3. Reductions with Aluminum

The use of untreated aluminum powder proved ineffective in producing a reduced complex. Likewise, concurrent use of HCl gas or tetrabutylammonium chloride in reduction reactions appeared to prevent the reaction from taking place. In the case of HCl it is clear that the gas competes with the titanocene dichloride in reaction with the aluminum metal. Tetrabutylammonium chloride is hygroscopic and difficult to dry prior to use in reactions. Since the reduced complexes and, indeed, the parent titanocene dichloride are hydrolyzed by water it is probable that hydrolysis reaction limits the formation of d products.

When the mercurous nitrate activated aluminum foil was stirred in the THF solution of titanocene dichloride for several hours under argon the red solution turned brownish green. After filtering in the dry box the solution produced a strong ESR signal and it was this solution which was then added to various concentrations of parent titanocene dichloride and produced the line broadening of the ESR signals, Figure 18. In addition, the mass spectrum of the solution shows that no dimerization has occured because no mass peaks appear above the parent complex at 249 mass units, Figure 19. Unfortunately the mass spectrum of the aluminum reduced solution can not be used to unambigously determine the nature of the reduced species because, if $[Cp_2TiCl_2]^-$ is present, it could produce the peak at approximately 248-249 units or some of the unreduced titanocene dichloride still in solution could also produce the same

Figure 17. Mass Spectrum of Zinc Reduced Titanocene Dichloride

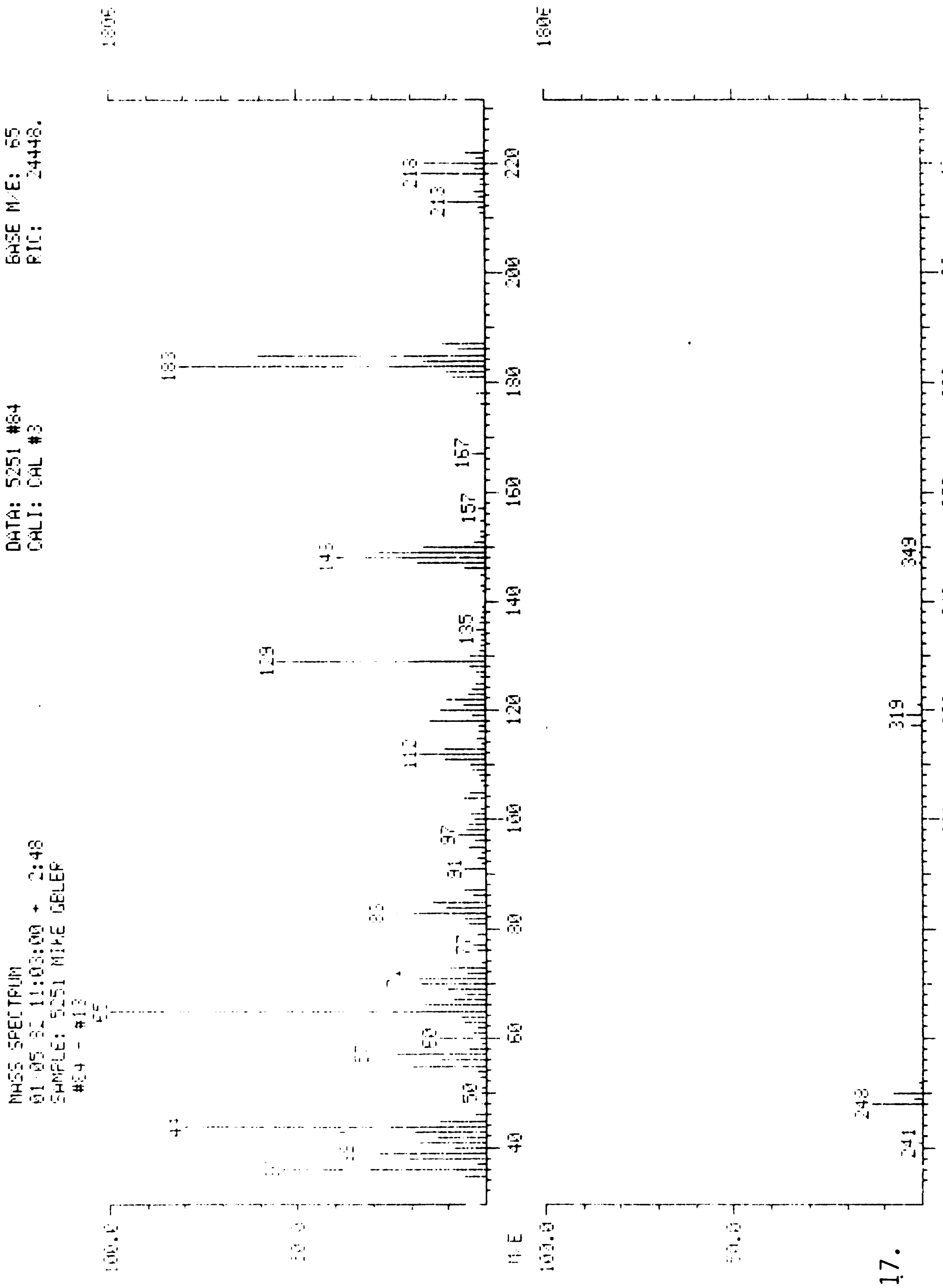


Figure 17.

Figure 18. ESR Signals of Aluminum Reduced Titanocene Dichloride with varying concentrations of unreduced Titanocene Dichloride.

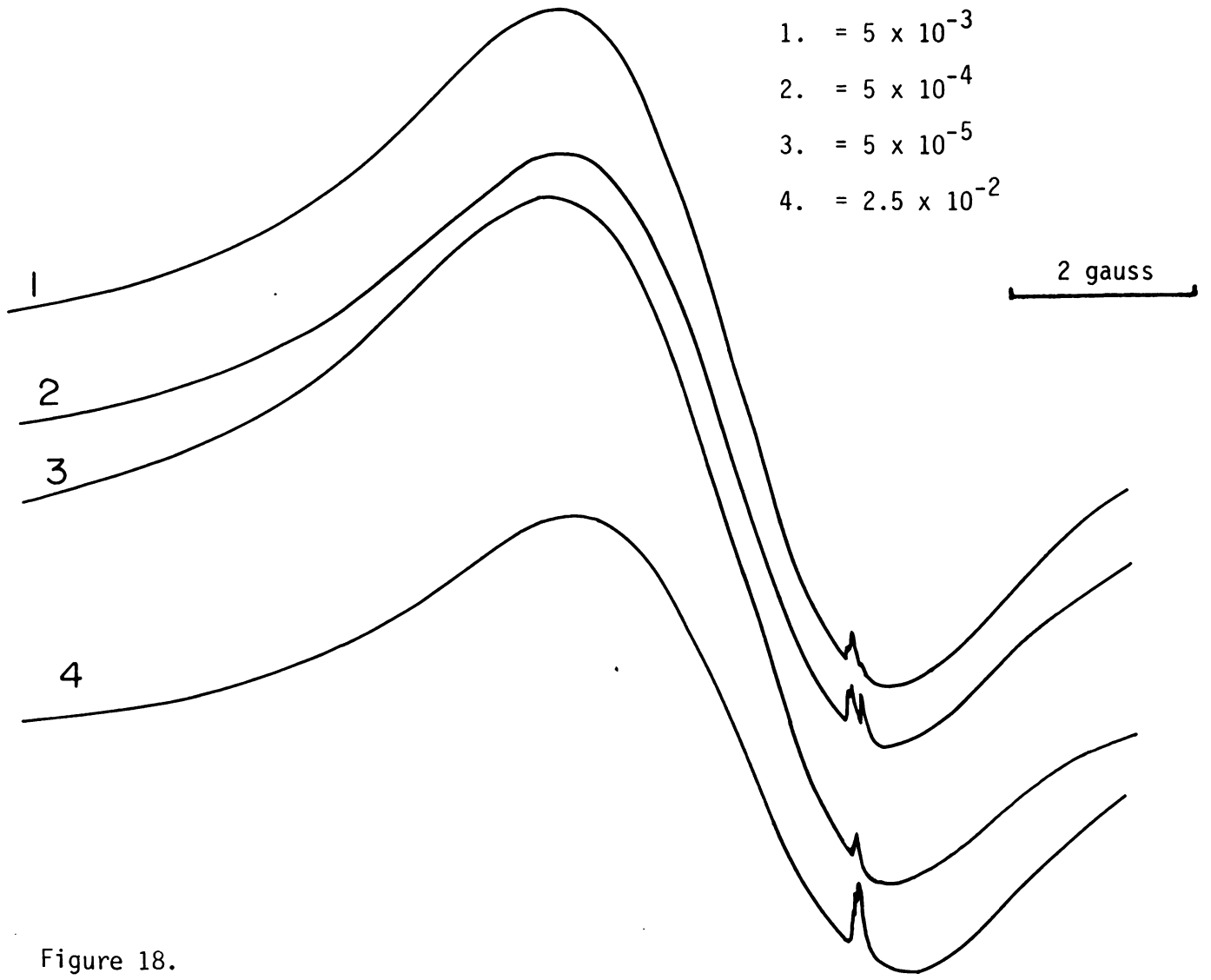
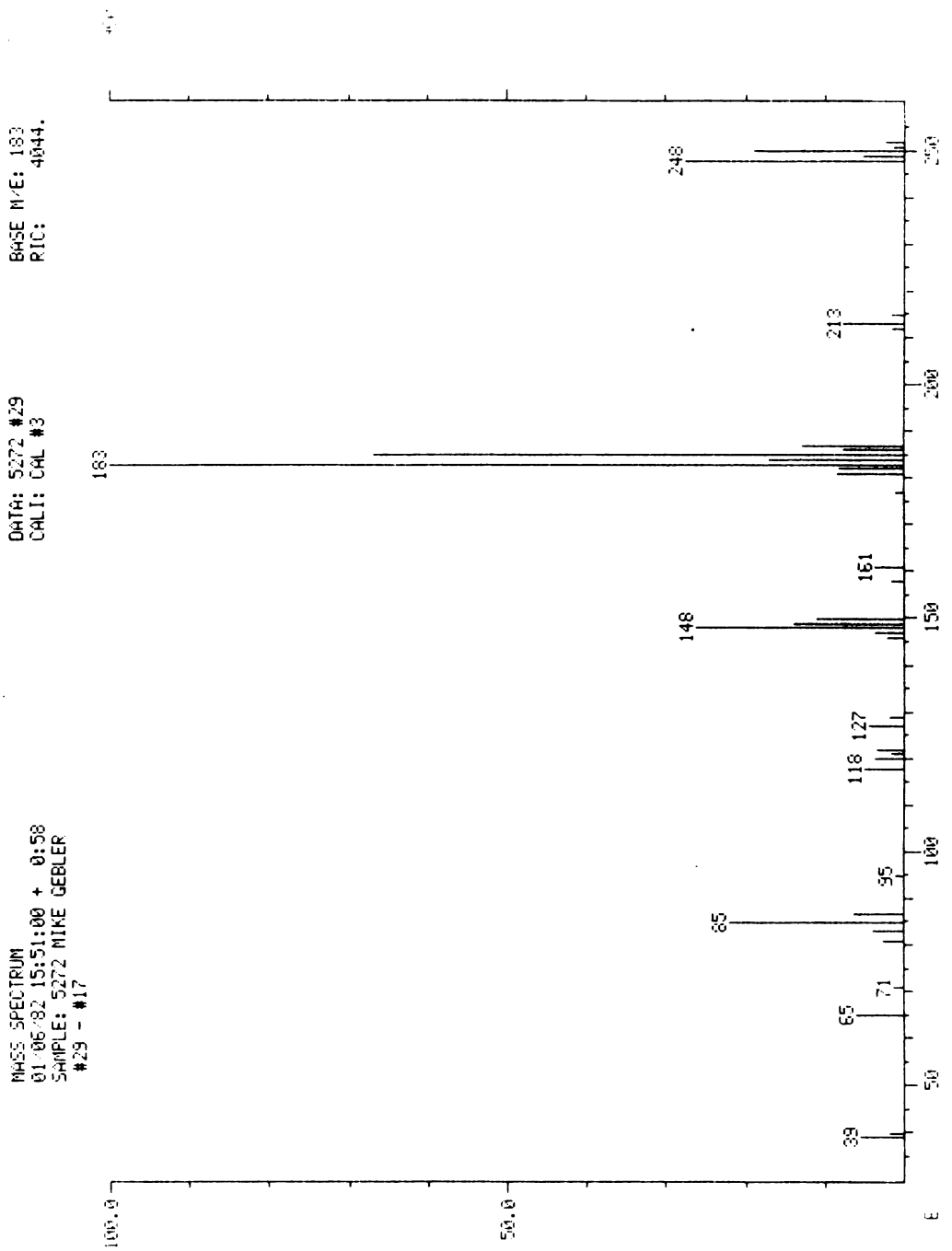

Parent Titanocene Dichloride (M)
1. = 5 x 10^{-3}
2. = 5 x 10^{-4}
3. = 5 x 10^{-5}
4. = 2.5 x 10^{-2}
2 gauss
1
2
3
4

Figure 18.

Figure 19. Mass Spectrum of Aluminum Reduced Titanocene Dichloride


MASS SPECTRUM
01/06/82 15:51:00 + 0:58
SAMPLE: 5272 MIKE GEBLER
#29 - #17
DATA: 5272 #29
CALI: CAL #3
BASE M/E: 183
RIC: 4044.
100.0
50.0
0
39
50
65
71
85
95
100
118
127
148
150
161
183
200
213
248
250

peak. Likewise the peak at 213 can be attributed to a reduced titanocene monochloride or simply to a chlorine atom cleavage from titanocene dichloride or reduced titanocene dichloride.

The rate of electron transfer is calculated in the usual manner[29-30] by utilizing the equation,

$$k = \frac{1.52 \times 10^7 \times \Delta H}{C}$$

where ΔH is the change of ESR linewidth in gauss and C is the concentration of the parent titanocene dichloride in molarity terms. The constant 1.52×10^7 is derived from the Bohr magneton, Plank's constant, and a standard g value compared to the formula for ESR relaxation times. Since H/C is the slope of the line from Figure 20, which equals -15.03 gauss/M, then, $k = 2.3 \times 10^8\ M^{-1}\ sec^{-1}$.

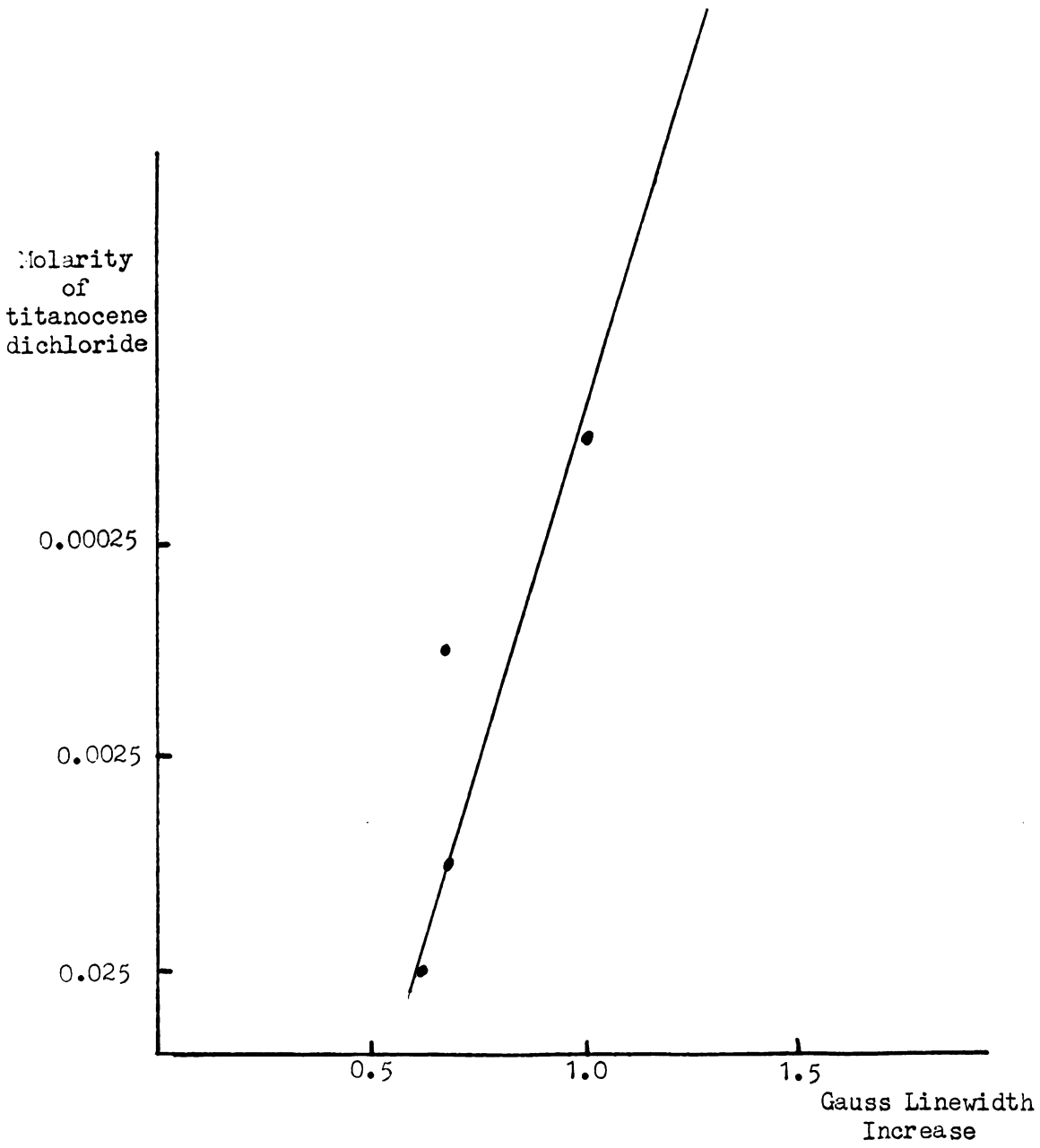


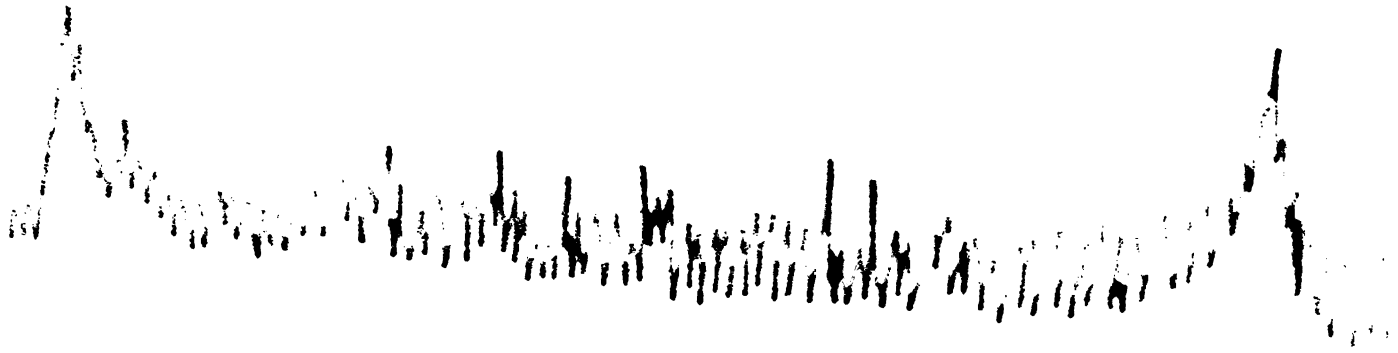
Figure 20. Variation of Linewidth of ESR Signals of Aluminum Reduced Titanocene Dichloride Treated with Unreacted Titanocene Dichloride

SUGGESTIONS

The exact composition of the Titanium (III) containing complex should be determined. This would require isolation of the complex from the reduction mixture of titanocene dichloride, aluminum, and aluminum chloride without further reaction or decomposition of the reduced compound.

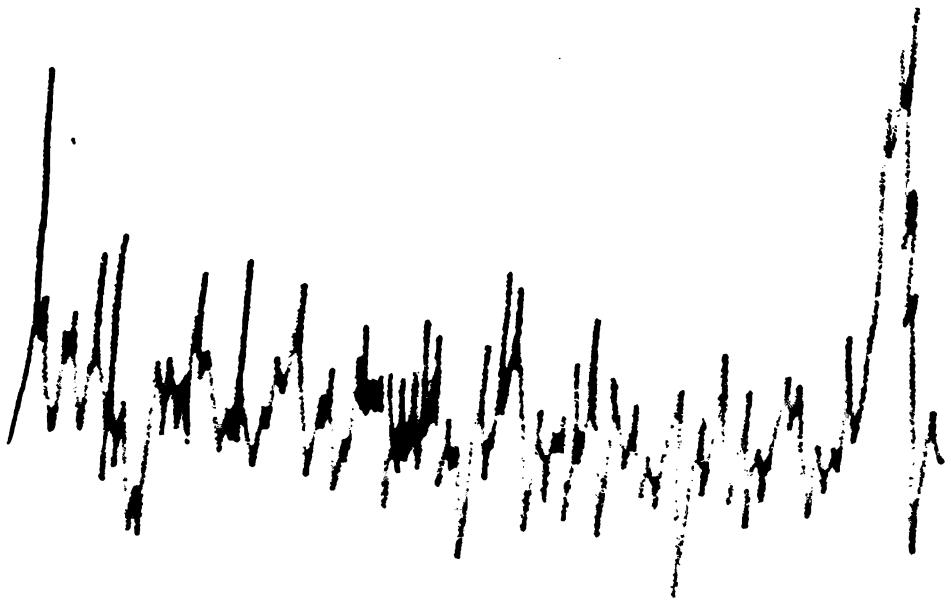
In addition, substituted biscyclopentadienyl complexes of titanium could be synthesized, reduced, and purified, used in line broadening experiments. Comparions of data obtained by these experiments would result in determination of many thermodynamic values for electron transfer reactions of these complexes by methods previously used on analogous systems.[29-30]

APPENDIX A



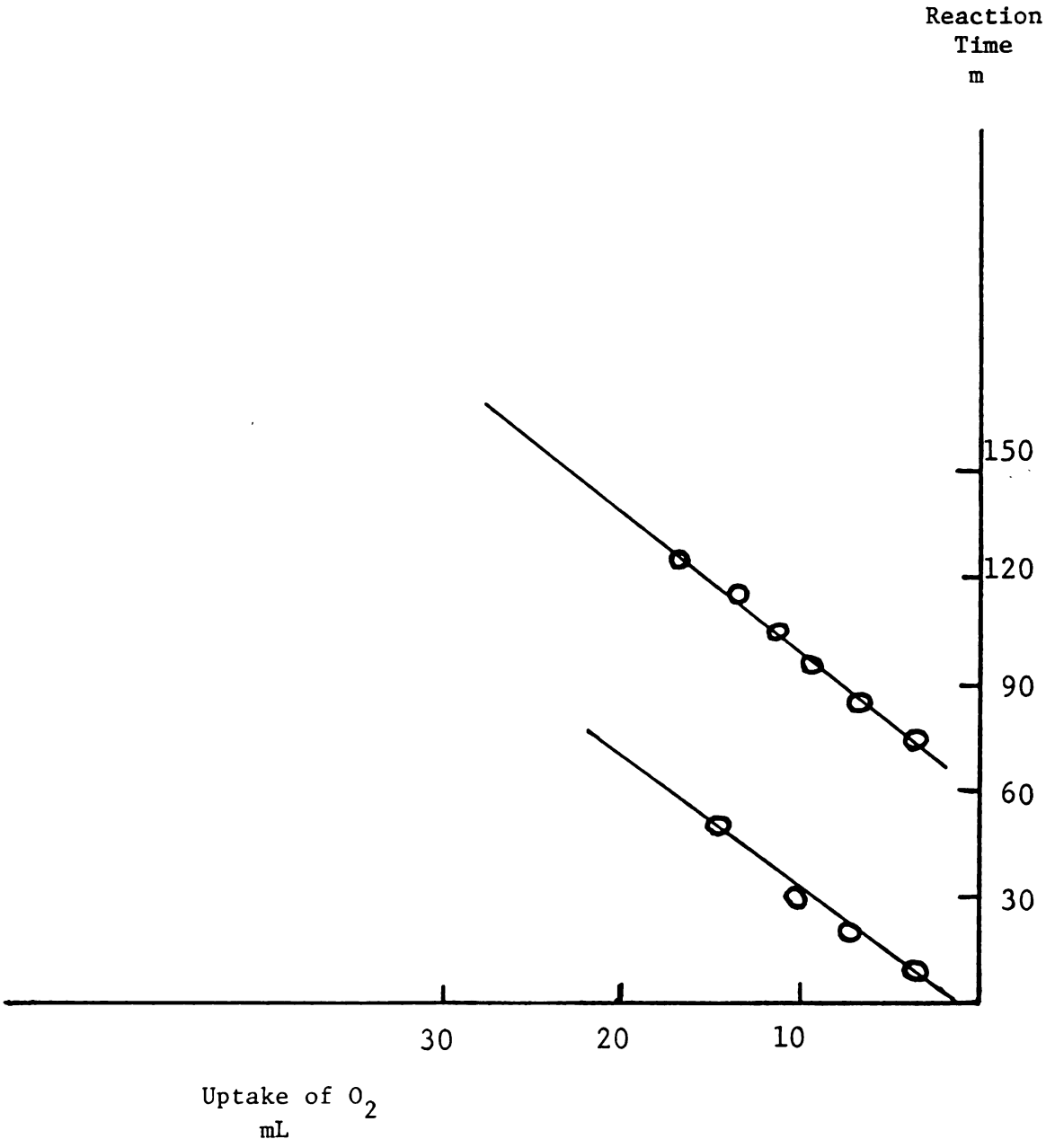
A.1. Iron Phthalocyanine Supported on 20% DVB-polystyrene, SEM Trace (Sulfonamide linkage)

A.2. Nickel Phthalocyanine Supported on 20% DVB-polystyrene, SEM Trace (Sulfonamide linkage)

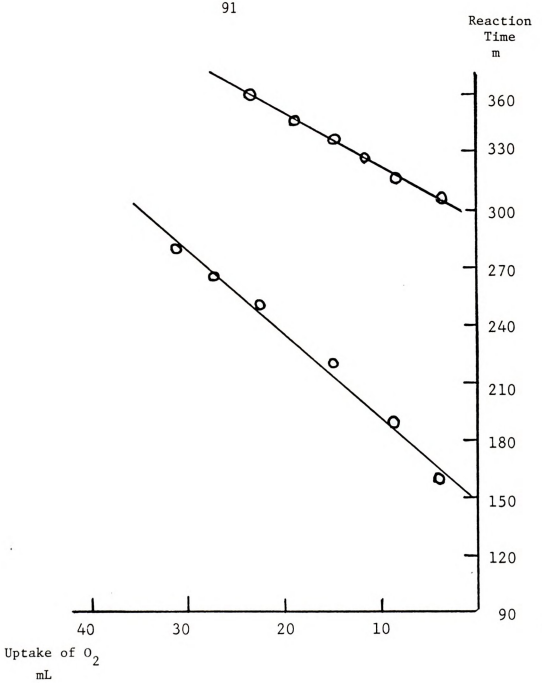


A. 3. Nickel Phthalocyanine Supported on 20% DVB-polystyrene. SEM Trace (Sulfone linkage)

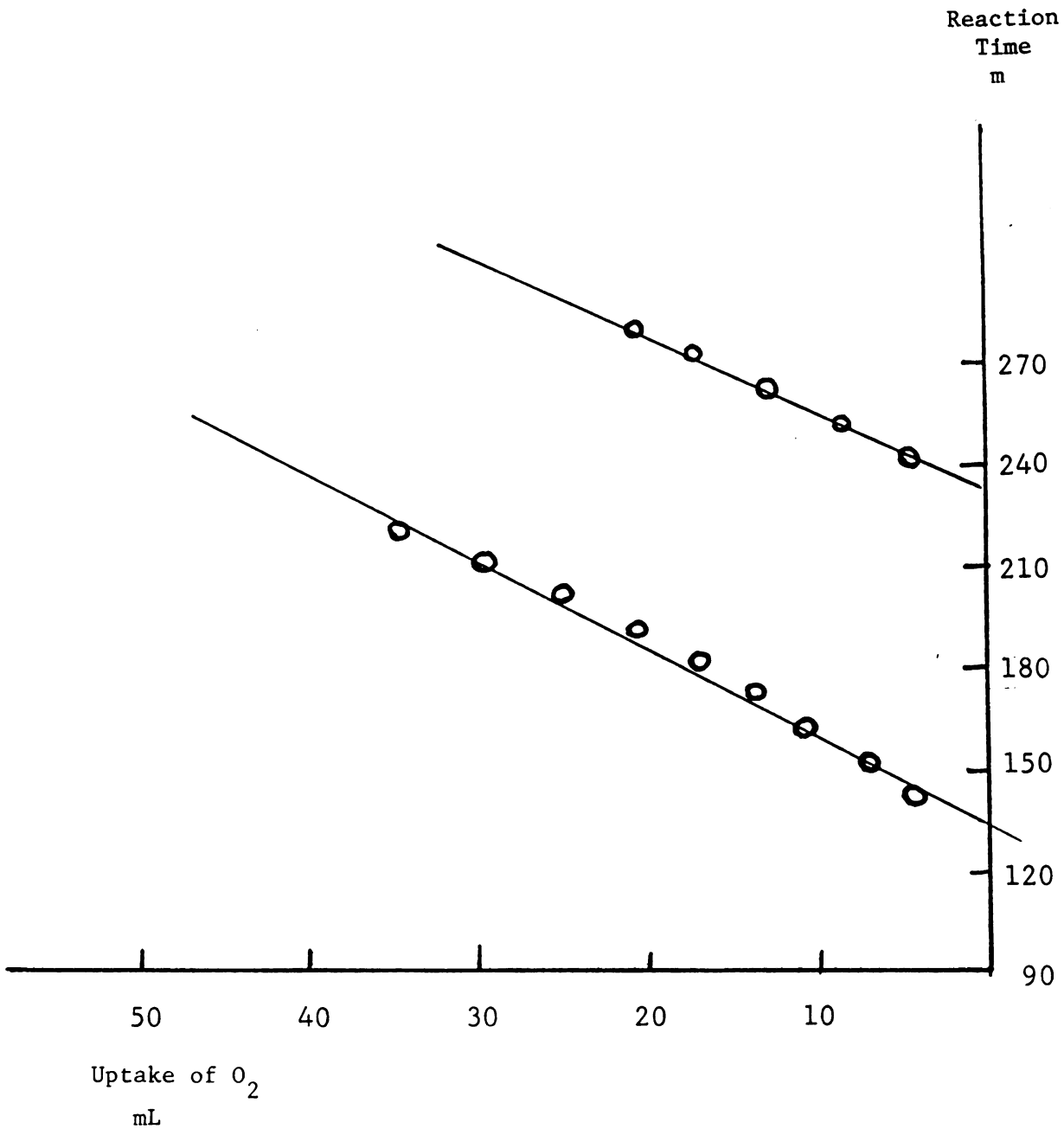
APPENDIX B



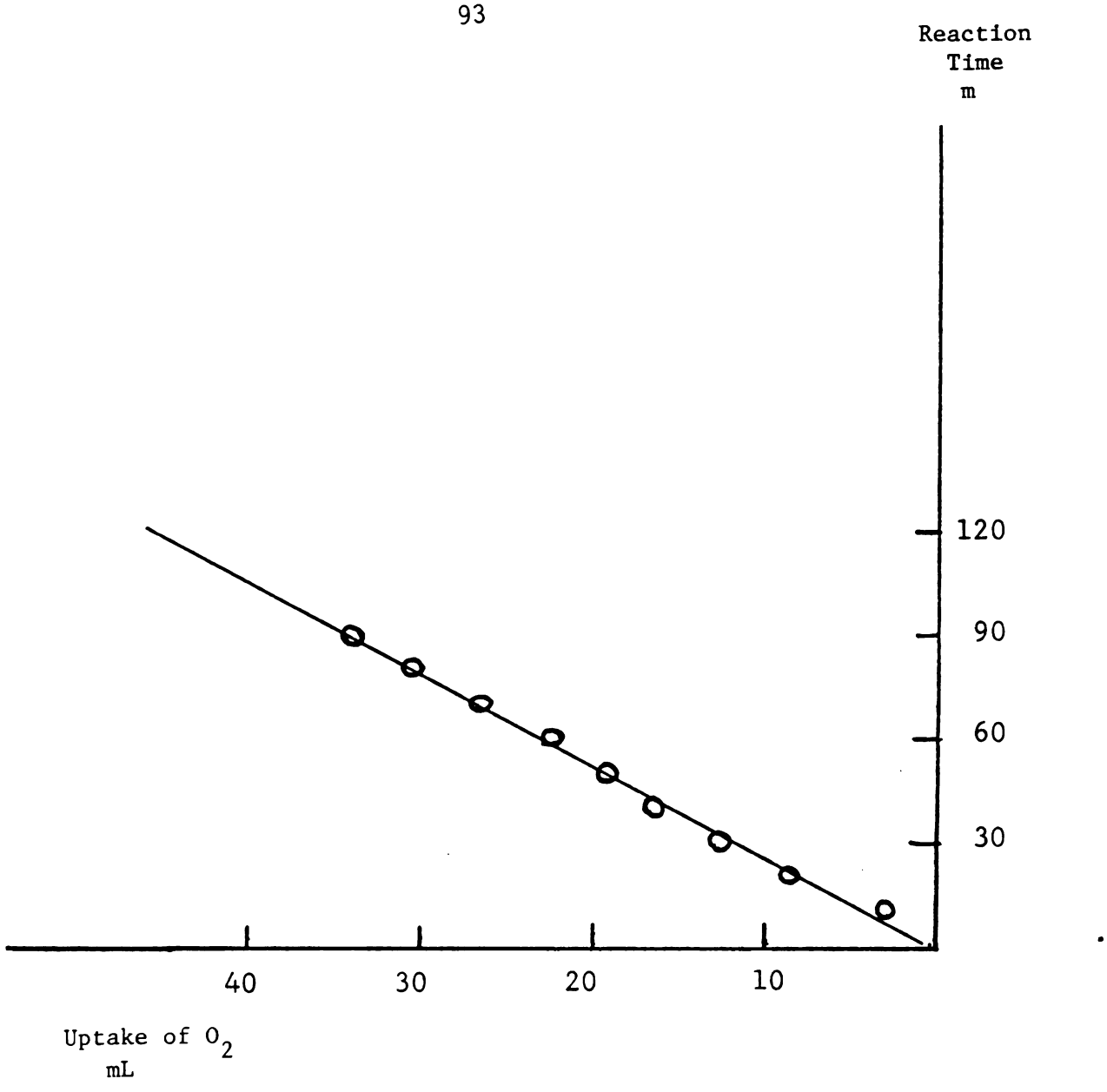
B.1. Polymer Supported NiPc (used) In Oxidation of Cyclohexene at 78°C (Graphs starts after incubation period of 16.75 h)



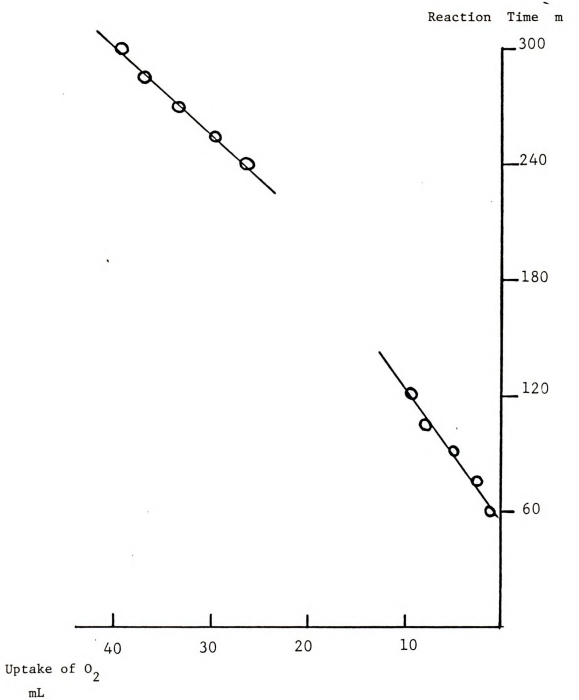
B.2. Polymer Supported NiPc (ground) In Oxidation of Cyclohexene at 78^{o} C



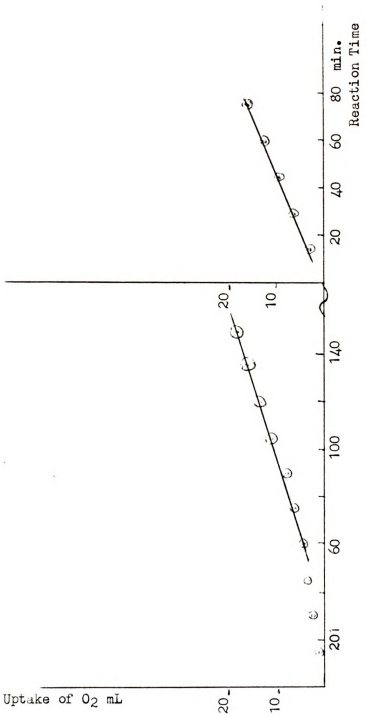
B.3. Polymer Supported VOPc (new) In Oxidation of Cyclohexene at 78°C



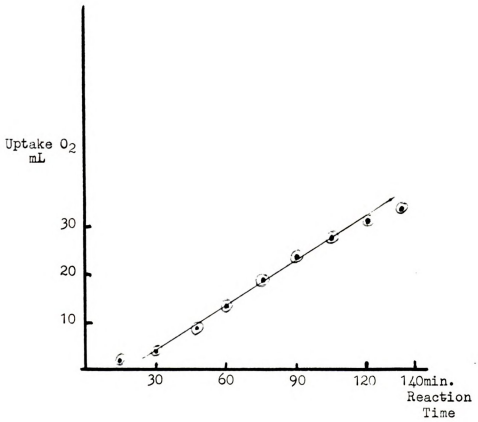
B.4. Polymer Supported VOPc (used) In Oxidation of Cyclohexene at $78^{o}C$ (Graph starts after incubation period of 15.5 h)



B.5. Polymer Supported NiPc in Oxidation of Cyclohexene with 1, 2 Dichloroethane Carrier



B.6. Polymer Supported MnPc in Oxidation of Cyclohexene
Sulfonamide linkage, New and Used



B.7. Polymer Supported CoPc in Oxidation of Cyclohexene. Sulfonamide linkage, New and Used

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