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KINETICS OF ELECTROCATALYSIS OF DIBROMOALKYL REDUCTIONS USING E-ETC(U)
JAN 81 R D ROCKLIN, R W MURRAY

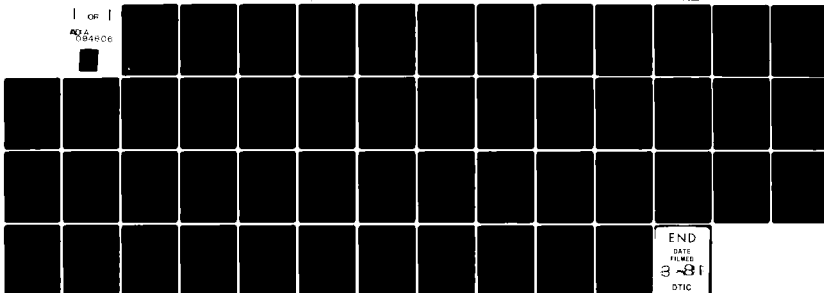
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KINETICS OF ELECTROCATALYSIS OF DIBROMOALKYL REDUCTIONS USING ELECTRODES
WITH COVALENTLY IMMOBILIZED METALLOTETRAPHENYLPORPHYRINS

by

Roy D. Rocklin and Royce W. Murray

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WITH COVALENTLY IMMOBILIZED METALLOTETRAPHENYLPORPHYRINS

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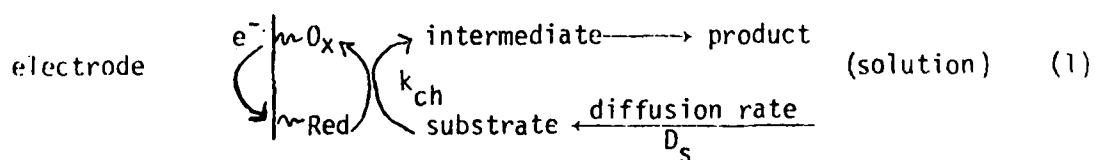
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ABSTRACT

The reduction of $\text{PhCHBrCH}_2\text{Br}$, PhCHBrCHBrPh , and $\text{CH}_2\text{BrCHBrCH}_3$ at the surfaces of electrodes to which cobalt(II) or copper(II) tetra(*p*-aminophenyl)-porphyrin had been covalently attached is strongly catalyzed by reduction of the metalloporphyrin. The rate of the electrocatalytic reduction was measured using rotated disk electrode voltammetry, and was independent of the amount of metalloporphyrin on the electrode above an estimated monomolecular coverage level. The results are consistent with theory which assumes that the rate of diffusion of electrochemical charge through the porphyrin layer is faster than the rate of diffusion of catalytic substrate through the layer. Comparison of the electrocatalytic rates for the different substrates indicates the electron transfer mediation involves specific interactions between substrate and metalloporphyrin rather than being a simple outer sphere electron transfer event. Potential step chronoamperometry is introduced as an alternative method for electrocatalytic measurements at modified electrodes.

There has been great interest over the past several years in bonding or coating monomolecular and multimolecular layers of chemicals on electrode surfaces so as to give the electrode special or distinctive characteristics. A number of chemical and physical preparative routes to such chemically modified electrode surfaces have been described.¹ Increasingly, efforts are being directed toward preparing surfaces which accelerate electrochemical reactions of substances dissolved in the contacting solution which are at naked electrode surfaces only slowly electrochemically oxidized or reduced. Such electrocatalysis normally involves redox transformations of the immobilized chemicals which mediate, in an outer sphere electron transfer step or in more complex reaction chemistry, the oxidative or reductive transfer of electrons between the electrode surface and the dissolved substrate. The two electrocatalytic situations have been termed, respectively, redox catalysis and chemical catalysis.^{2,3} Mediated electrocatalysis is, for reduction, represented by the general scheme

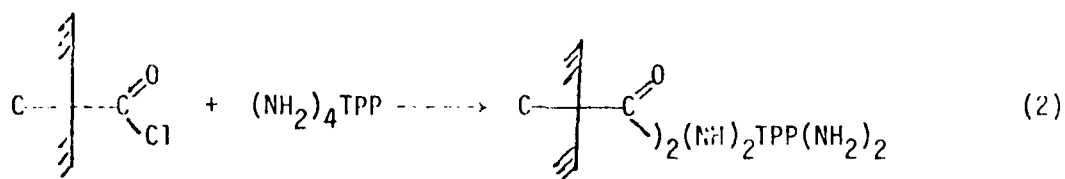


where Ox/Red is the immobilized redox couple of which Red reacts with substrate at rate k_{ch} to give a product which is rapidly and irreversibly transformed into another product.

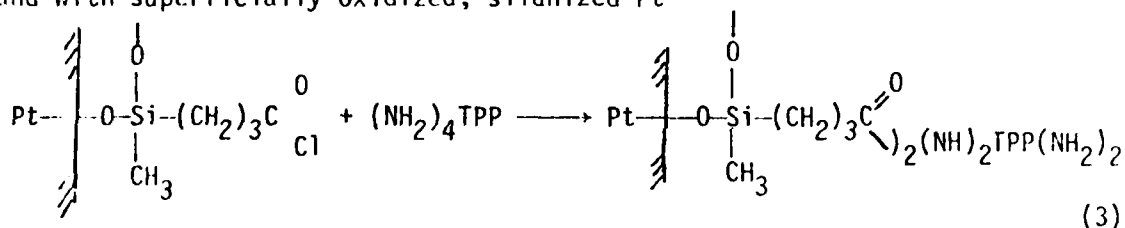
Interesting and imaginative, but qualitative, illustrations of this scheme have been successfully achieved,⁴⁻¹² whereas quantitative electrocatalytic studies and measurements of k_{ch} are scarce. Oyama and Anson^{6a} have measured k_{ch} between dissolved metal complexes and IrCl_6^{3-} trapped in an

anion exchange film coated on a rotated carbon disk, and Lewis, et al.^{5a} have measured k_{ch} between ferricenium photogenerated in a polymer film and iodide in solution. Cyclic voltammetry theory has been presented for reaction 1 but without illustrative experiments.²

We have described procedures for immobilizing tetra(p-aminophenyl)-porphyrins $(\text{NH}_2)_4\text{TPP}$, by reacting it with thionyl chloride-treated glassy carbon.^{11a,13}



and with superficially oxidized, silanized Pt¹⁴



Two surface amide bonds (on the average) are formed in reactions 2 and 3^{13c,14a}, the products of which we abbreviate, respectively, as C/ $\sim$ (NH₂)₄TPP and Pt/ $\sim$ (NH₂)₄TPP, and which can be subsequently metallated, to C/ $\sim$ (M)(NH₂)₄TPP and Pt/ $\sim$ (M)(NH₂)₄TPP, where M = Co, Cu, Zn, and Mn^{11a} among others.

These porphyrin electrode surfaces have proven to be electrocatalytically active toward reduction of alkyl bromides which are classically slowly introduced at naked electrodes.¹⁶ The electrocatalytic activity is rapidly degraded during reductions of monobromo species, but several 1,2-dibromoalkyl substrates exhibited sufficient stability for quantitative kinetic studies, which were undertaken. We report here measurements of catalytic rate as a

function of substrate, of metal, and of porphyrin coverage as attained in reaction 3 from submonomolecular to multimolecular. Most of the rate measurements were performed with rotated disk electrode voltammetry; in the interests of testing new methodology some were carried out with potential step chronoamperometry. The dibromo substrates used are 1,2-dibromo-1,2-diphenylethane (PhCHBrCHBrPh), 1,2-dibromophenylethane ($\text{PhCHBrCH}_2\text{Br}$), and 1,2-dibromopropane ($\text{CH}_2\text{BrCHBrCH}_3$). The results for reduction of $\text{PhCHBrCH}_2\text{Br}$ show that the catalytically reactive zone on $\text{Pt}/\sim(\text{Co})(\text{NH}_2)_4\text{TPP}$ and $\text{Pt}/\sim(\text{Cu})(\text{NH}_2)_4\text{TPP}$ electrodes is the outermost layer of porphyrin sites.

EXPERIMENTAL

Chemicals. Meso-tetra(p-aminophenyl)porphyrin, $(\text{NH}_2)_4\text{TPP}$, was synthesized by the Adler method,¹⁵ refluxing equimolar amounts of pyrrole and p-acetamidobenzaldehyde (ca. 5 g.) in 250 ml propionic acid for 30 min., then adding 250 ml concentrated HCl to the cooled solution and refluxing again to hydrolyze the acetyl grouping. Cooling the solution in an ice-bath and neutralizing with aqueous ammonia gives a brown precipitate which was filtered, air dried, and extracted with tetrahydrofuran. The extract was concentrated to 50 ml and 500 ml diethyl ether added, precipitating impurities. The deep red solution was filtered, concentrated, and chromatographed on a silica gel column with 95% CH_2Cl_2 /5% CH_3OH ; taking the central band fraction to dryness and extracting with CH_2Cl_2 was followed by final chromatography on a short silica gel column with 99% CH_2Cl_2 /1% CH_3OH .

$\text{PhCHBrCH}_2\text{Br}$ was recrystallized twice from 2-propanol and PhCHBrCHBrPh once from acetone. $\text{CH}_2\text{BrCHBrCH}_3$ was washed with concentrated H_2SO_4 , neutralized with Na_2CO_3 , washed with water, dried with MgSO_4 , and fractionally

distilled. The electrochemical solvent dimethylsulfoxide, DMSO, was dried over Linde 4 Å molecular sieves and contained 0.1 M tetraethylammonium perchlorate supporting electrolyte.

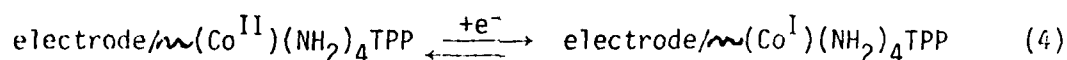
Electrodes. Glassy carbon electrodes were polished on the cylinder ends (0.06 cm.^2), finishing with 1 micron diamond paste. The porphyrin was attached by refluxing the electrodes with 1-2 ml freshly distilled thionyl chloride in 15 ml Na° dried toluene, briefly rinsing, then two hours exposure to a refluxing solution of ca. 1 mg porphyrin in 15 ml toluene. The metals were inserted in refluxing DMF solutions of the metal(II) chloride for 15 minutes followed by washing in DMF, CH_3OH , air drying, and mounting on a brass holder with heat-shrink Teflon.

One micron diamond paste polished Pt disks (0.1 cm.^2), Teflon shrouded, were modified by placing a drop of neat 4-methyldichlorosilylbutyryl chloride on the surface in room air for one minute, briefly rinsing in toluene, and exposure to a hot toluene solution (5 ml) containing ca. 1 mg porphyrin. The porphyrin surface was metallated with cobalt by warming the electrode to either 75°C or 90°C for 6 hours in a DMF solution of CoCl_2 . Copper was inserted by warming the silanized electrode to ca. 50°C in a DMF solution of CuCl_2 for 1 hour.

Electrochemical experiments. Electrochemical equipment and cells were of conventional design. Prior to measurement of electrocatalytic currents the porphyrin coated electrode was inspected with cyclic voltammetry to measure the porphyrin coverage from its electrochemical wave. Rotated disk experiments were conducted with a Pine Instruments rotator, and limiting current values were typically taken at a fixed potential on the catalytic wave plateau. Electrode potentials are referenced to a NaCl saturated SCE (SSCE).

RESULTS AND DISCUSSION

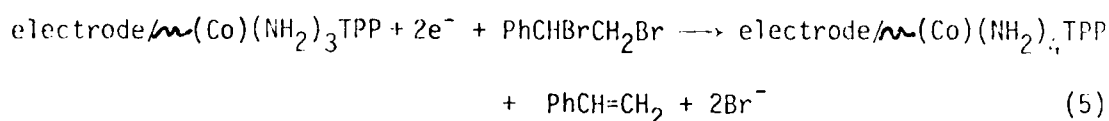
Cyclic Voltammetry. Cyclic voltammetry is a useful qualitative tool to ascertain the existence and stability of catalysis for a given metalloporphyrin-substrate combination. Results with C/ $\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$ and Pt/ $\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$ surfaces and PhCHBrCH₂Br substrate are shown in Figure 1. The immobilized metalloporphyrin wave, corresponding to the reaction ($E_{\text{surf}}^{\circ} = -0.86$ volt vs. SSCE) (Curves A,D)



is determined in the absence of substrate to assess the total coverage of porphyrin on the electrode, Γ_T , and additionally after electrocatalysis experiments, to inspect for surface degradation. Quantitative kinetic data are reported here only when the electrode degradation has been minimal (< 20% change).

In the absence of immobilized porphyrin, Figure 1, Curves C,F, show that PhCHBrCH₂Br is reduced on naked glassy carbon and Pt in a drawn out, wave at ca. -1.4 volt vs. SSCE. Significantly, silanization of the Pt causes little change in Curve F. Using electrodes to which cobalt-metallated porphyrin has been attached causes a strong voltage catalysis, shifting the PhCHBrCH₂Br reduction by 560-600 mv, Curves B,E. Judging from the relative heights of the catalyzed and uncatalyzed waves in Figure 1, and the absence of any anodic wave for reaction 4 in the presence of PhCHBrCH₂Br, the catalysis is fast, occurring at or near a diffusion controlled rate. The catalyzed reaction occurs near the potential for reaction 4, as expected if the reduced form of the porphyrin acts to transfer electrons to the substrate. Reductions

of 1,2-dibromoalkyls are known^{16,17} to yield olefins, and Miller^{9a,b} has demonstrated that the electrocatalytic reduction of $\text{PhCHBrCH}_2\text{Br}$ by a poly-(*p*-nitrostyrene) film on a electrode yields styrene as product. These porphyrin surfaces are however not sufficiently stable for product analysis studies, and so we assume by analogy with the earlier work that the electrochemical reaction in Figure 1 has the stoichiometry



Reduction of $\text{PhCHBrCH}_2\text{Br}$ is also catalyzed by a porphyrin surface which has been metallated with Cu, giving a current peak near $E_{\text{surf}}^{\circ'}$ for this metalloporphyrin, -1.21 volt, and by porphyrin surfaces which have not been metallated at all. In the latter, free base porphyrin catalysis, in contrast to the Co and Cu examples, the electrocatalytic effect persists only for a small number of cyclical potential scans, making quantitative experiments impossible. The Co and Cu porphyrin electrodes are sufficiently stable for quantitative rotated disk and chronoamperometric kinetic studies.

Results for reduction of PhCHBrCHBrPh and $\text{CH}_2\text{BrCHBrCH}_3$ are given in Figures 2 and 3. For PhCHBrCHBrPh , electrocatalysis occurs with the free base (again unstable) and cobalt metallated porphyrin, whereas manganese porphyrin is ineffective. For $\text{CH}_2\text{BrCHBrCH}_3$, reduced at a rather negative potential on naked Pt, only the cobalt porphyrin shows any activity. The mechanistic implication of these results, summarized in Table I, is considered later.

Rotated Disk Voltammetry Limiting Current Theory. For this technique, the published relationship is^{6,18}

$$\frac{1}{i_{\max}} = \frac{1}{nFAk_{\text{ch}}C_S} + \frac{1}{0.62nFAD_S^{2/3} \nu^{-1/6} \omega^{1/2} C_S} \quad (6)$$

where $i_{\max}$ is the limiting current of the electrocatalyzed wave, k_{ch} ($\text{cm}^3/\text{mole}\cdot\text{sec.}$) is the rate constant for the reaction of substrate (concentration C_S , mole/cm^3) with reduced porphyrin sites according to the rate law $-dI/dt = k_{\text{ch}}I'C_S$, D_S is the diffusion coefficient of substrate in the solution, and ω is the rate of electrode rotation in $\text{rads}/\text{sec.}$ This equation predicts that at the $1/\omega^{1/2} = 0$ intercept of a $1/i_{\max}$ vs. $1/\omega^{1/2}$ plot, called a Koutecky-Levich plot¹⁸, the current is limited solely by the rate of substrate-reduced porphyrin chemical reaction and not by the mass transport of substrate from the solution to the rotated electrode. Equation 6 has been applied by Oyama and Anson^{6a} and by Alberly et al¹⁹ in modified electrode studies.

By manipulating the conditions of Pt electrode silanization preceding Reaction 3 so as to produce a siloxane polymer film with reactive acid chloride sites, it is possible to increase the coverage of porphyrin catalyst sites bound via Reaction 3 above a monomolecular and submonomolecular level to as much as ca. 2×10^{-9} mole/cm^2 . For electrocatalysis on electrodes covered with polymeric, multimolecular layer films, equation 6 neglects two additional reaction steps. In one, reduced porphyrin catalyst sites migrate outward from the electrode through the polymer film toward incoming substrate, by electron self exchange^{20,21} between neighboring oxidized and reduced porphyrin sites. There is now strong evidence^{20,22-25},

despite suggestions to the contrary^{9d}, that the rate of this migration of electrochemical charge can be expressed as a Fickian charge transport process with diffusion constant D_{ct} (cm.²/sec.). The second reaction step is the diffusion of substrate through the polymer film toward reduced porphyrin sites, expressed by the rate $D_{S,pol}$ in cm.²/sec. Thus, three reaction steps, charge transport, substrate diffusion, and the chemical reaction, occur within the polymer film and may influence the value of $1/i_{max}$ at $1/\omega^{1/2} = 0$.

Theory accounting for all these reaction steps is not available. Andrieux and Saveant²⁶ considered, and dismissed, cyclic voltammetric current limitation due to diffusion of substrate in a multilayer film, concluding that (under specified conditions) current was controlled by substrate reacting, more or less uniformly, with all catalyst sites in the film (i.e., $\Gamma = \Gamma_T$). Anson^{6b}, considering charge transport and (outer sphere) chemical rates, concluded that in most cases charge transport was unlikely to control the current, and again that $\Gamma = \Gamma_T$. These studies omitted consideration of the third factor of charge transport and substrate diffusion, respectively. In several experimental studies of electrocatalysis^{62,9d}, including this one, however, the apparent chemical reaction rate was not proportional to Γ_T , and effect not accounted for by these theories, but which can be explained by elementary theory which follows.

Consider²⁷ the three reaction steps in terms of their flux (mole/cm.²sec.) when current-controlling, $(CT \text{ flux})_{lim}$, $(CHEM \text{ flux})_{lim}$, and $(SUBS \text{ flux})_{lim}$, and when one of the other steps dominates, $CT \text{ flux}$, $CHEM \text{ flux}$, and $SUBS \text{ flux}$, all at the $1/\omega^{1/2}$ intercept. The current is

necessarily equated to the steady state flux of reduced catalyst sites, i.e., the charge transport rate,

$$\frac{i_{\max}}{nFA} = \text{CT flux} = \frac{D_{\text{ct}}[C_{\text{TPP}}(x=0) - C_{\text{TPP}}(x=p)]}{p} \quad (7)$$

where C_{TPP} is the concentration of reduced porphyrin catalyst sites (at $x=0$, $C_{\text{TPP}} = \Gamma_T/d$, where d is film thickness) and $p \leq d$ is a distance interval in the film over which a C_{TPP} gradient exists. If $i_{\max}$ is controlled by the charge transport rate, equation 7 becomes

$$(\text{CT flux})_{\text{lim}} = \frac{D_{\text{ct}} C_{\text{TPP}}(x=0)}{d} = \frac{D_{\text{ct}} \Gamma_T}{d^2} \quad (8)$$

The flux of substrate consumed by the chemical reaction, CHEM flux, is equal to CT flux, and if it is limiting,

$$(\text{CHEM flux})_{\text{lim}} = k_{\text{ch}} \Gamma C_S \quad (9)$$

and equation 6 results. Note that in equations 6 and 9, Γ is the coverage of catalyst sites which actually undergo reaction with substrate and not presumed equal to Γ_T .

The flux of substrate SUBS flux diffusing into the polymer film to be consumed by catalyst sites must be equal to both CHEM flux and CT flux and is given by

$$\text{SUBS flux} = \frac{D_{\text{S,pol}}^P [C_S(x=d) - C_S(x=q)]}{d-q} \quad (10)$$

where $C_{S(x)}$ is the concentration of substrate in the polymer film forming a gradient over the distance interval $d-q$, and P is the partition coefficient with which substrate dissolves into the polymer film from the solution. The product $D_{S,pol}P$ can be small, especially if entrance of substrate into the polymer film is made unfavorable by substrate charge (ion exchange film co-ion exclusion) or molecular size considerations. It is physically reasonable, however, to assume that the electrocatalysis can proceed even if $D_{S,pol}P$ is very small, since substrate need not diffuse within the polymer film to react with catalyst sites accessible at the polymer/solution interface.

Keeping in mind that one of the reaction fluxes can limit the others, which can force $p < d$ in equation 7 and $d-q < d$ in equation 10, the flux relationships can be employed to estimate steady state concentration distance profiles within polymer films on rotated disk electrodes. Six limiting conditions are conceivable according to the ordering of the three fluxes; four are shown in the diagrams of Figure 4. A fifth condition, SUBS > CT > CHEM flux, is like Panel B. The parameters chosen to estimate these diagrams, $D_{ct} = 10^{-12}$ to 4×10^{-10} cm.²/sec., $D_{S,pol} = 10^{-6}$ to 10^{-9} cm.²/sec., and $k_{ch} \Gamma C_S = 10^{-4}$ to 10^{-8} mole/cm.²sec. (corresponding to $10^3 k_{ch} = 10^4$ to 10^9 l./mole, sec) have values reasonably expectable under various circumstances of polymer film structure and reactivity, and lie within or near the values chosen by Anson^{6b} (except for $D_{S,pol}P$ which Anson did not examine). The values of limiting flux furthermore all lie within or near those measurable^{6b} at useful values of ω ($10 - 10^3$ rads/sec.) of the rotated disk electrode. The instructive aspect of Figure 4, in Panels A, C, and D, is that the zone of catalytic sites where substrate is consumed

can become quite narrow so that $\Gamma \ll \Gamma_T$. Only when $D_{S,pol}P$ is large (Panel B) or CHEM flux is small, do catalyst sites throughout the film participate in the reaction with substrate so that $\Gamma \sim \Gamma_T$. The diagrams in Figure 4 illustrate the necessity of considering three rather than two reaction steps to appreciate the potential range of electrocatalytic behavior of electrodes coated with multimolecular layers of catalyst sites.

The diagrams in Figure 4 furthermore suggest a reformulation of the $1/\omega^{1/2}$ intercept term of equation 6. In an impedance sense, comparison of Panels A, B, and C in particular suggest that the charge transport and substrate diffusion steps be expressed as elements which are in parallel with one another, this parallel combination being in series with the chemical step, which yields the revised intercept term

$$\frac{1}{nFAk_{ch}I^0C_S} + \frac{1}{nFAD_{S,pol}PC_{S(x=d)}/d + nFAD_{ct}\Gamma_T/d^2} \quad (11)$$

This relationship is approximate in several respects, but nonetheless can serve to anticipate functional dependencies on C_S , d , etc., to detect various forms of rate control of electrocatalytic currents by one or a combination of the three reaction steps discussed above. In limiting forms, equation 11 represents Panels A, B, and C, and Panel D approximately, in Figure 4, and we have preliminarily discussed some of these limits²².

The Rising Part of the Rotated Disk Electrocatalytic Wave. Assuming that the chemical reaction flux is the controlling reaction step (i.e., equation 6), and that the porphyrin sites on the electrode surface are, activity-wise, non-interacting so that the potential dependency of reduced porphyrin sites is

$$E = E_{\text{surf}}^{\circ'} + \frac{RT}{nF} \ln \frac{\Gamma_T - \Gamma_R}{\Gamma_R} \quad (12)$$

where $E_{\text{surf}}^{\circ'}$ is the formal potential of the porphyrin surface wave and Γ_R is coverage of reduced sites, the catalytic wave equation resulting is

$$E = E_{\text{surf}}^{\circ'} + \frac{RT}{nF} \ln \left[1 + \frac{k_{\text{ch}} \Gamma}{0.62 D_S^{2/3} \nu^{-1/6} \omega^{1/2}} \right] + \frac{RT}{nF} \ln \left[\frac{i_{\text{max}} - i}{i} \right] \quad (13)$$

Equation 13 predicts the shape of the electrocatalytic wave (plot E vs. $\ln[(i_{\text{max}} - i)/i]$) and that $k_{\text{ch}} \Gamma$ can be obtained from $E_{1/2}$. The difficulty with equation 13, as we shall see, is that the population of reduced porphyrin sites increases more gradually with potential than given by equation 12, as is typical of electrode immobilized chemicals¹.

Rotated Disk Electrode Voltammetry, Kinetic Measurements. The electrocatalytic reduction of $\text{PhCHBrCH}_2\text{Br}$ using a $\text{Pt}/\omega(\text{Cu})(\text{NH}_2)_4\text{TPP}$ surface is shown in Figure 5. Measuring i_{max} at constant potential (-1.3 volt vs. SSCE) to ensure steady state conditions gives the i_{max} data compared to ω , according to equation 6, in Figure 6. The non-zero intercept of Figure 6 shows the $\text{PhCHBrCH}_2\text{Br}$ reduction is not mass transfer controlled, but is limited by the kinetics of the electrocatalytic process. Also shown in Figure 6 are results at other substrate concentrations C_S , which show that the slope and intercept of these Koutecky-Levich plots are inversely proportional to $[\text{PhCHBrCH}_2\text{Br}]$ as expected from equations 6 and 11 if charge transport through the porphyrin film is not rate limiting. The slope of Curve B, Figure 6, yields $D_S = 3.5 \times 10^{-6} \text{ cm}^2/\text{sec}$. which agrees with a direct chronoamperometric (Cottrell plot) measurement of $D_S = 3.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ on a naked Pt electrode using potential step to

-1.65 volts (diffusion controlled for the uncatalyzed reaction).

Data taken from the intercepts of plots like Figure 6 (Entries 1-3) and others taken at different temperatures, are collected in Table II, expressing the intercept as $k_{ch}\Gamma$ using equation 6. A striking aspect of these data is that $k_{ch}\Gamma$ is not proportional to the total coverage of porphyrin Γ_T but in fact seems independent of it. Note the greater than four-fold changes in Γ_T in Entries 1-3 and in 4-7 where $k_{ch}\Gamma$ varies only by small amounts. On electrodes prepared by Reaction 3, we have shown elsewhere that the immobilized porphyrin is electrochemically quantitatively reducible^{14a}, so the increases in Γ_T are in fact larger populations of reduced, active porphyrin catalyst to the electrode surface. Since film thickness presumably also increases with Γ_T , control of the Figure 6 intercepts by diffusion of $\text{PhCHBrCH}_2\text{Br}$ in the polymer film (i.e., SUBS flux) seems ruled out by the intercept's lack of response to Γ_T . If the intercept data are analyzed using equation 6, as done in Table II, the conclusion seems evident that the substrate reacts with only a fraction of the porphyrin sites. This conclusion is supported by data derived from $\text{Pt}/\omega(\text{Co})(\text{NH}_2)_4\text{TPP}$ electrocatalysis of this substrate, presented below.

Table II contains results for $k_{ch}\Gamma$ over the temperature range 20-50°C which, if plotted as $\ln[k_{ch}\Gamma]$ vs. $1/T$ using examples at constant Γ_T (Entries 2,5,8-10) yield a linear thermal barrier plot with $E_a = 5.6$ kcal/mole and frequency factor $Z = 160$ cm/sec. That both E_a and Z are fairly small is interesting but these results must be considered at best approximate given the scatter in $k_{ch}\Gamma$ of Table II.

The (in)dependency of $k_{ch}I'$ on I_T was studied further using the electrocatalytic reduction of 1 mM PhCHBrCH₂Br solutions by a series of Pt/ ω -(Co)(NH₂)₄TPP surfaces which were prepared so as to bear a range of coverages lower than those conveniently prepared using copper, and specifically encompassing values we believe submonomolecular and multimolecular levels. The Koutecky-Levich plots for the Pt/ ω -(Co)(NH₂)₄TPP-PhCHBrCH₂Br reaction are similar to those of Figure 6 and their slopes produce similar results for D_S , e.g., 2.6×10^{-6} cm.²/sec. The results for $k_{ch}I'$ differ slightly according to the cobalt metallation reaction temperature but as shown in Figure 7, electrodes metallated 75°C and 90°C display the same general trend. At low coverage, $k_{ch}I'$ increases with I_T , but levels off at ca. 1×10^{-10} mole/cm.² and becomes relatively independent of I_T as was the case for Pt/ ω -(Cu)(NH₂)₄TPP surfaces (Table II).

We interpret these results as follows. The reagent Cl₂Si(CH₃)(CH₂)₃-COCl, forming only linear siloxane polymer during the Pt electrode silanization, allows PhCHBrCH₂Br to readily diffuse through this film to the Pt surface²⁸. Incorporation of tetra(p-aminophenyl)porphyrin into this film, cross-linking the film by forming an average of two amide bonds per site^{14a}, lowers either the partition coefficient (P) for PhCHBrCH₂Br entering the film from the solution, or the rate at which PhCHBrCH₂Br diffuses ($D_{S,pol}$) into (and in) the film, or both. In the cross-linked film, if the SUBS flux of PhCHBrCH₂Br which enters the film, and the flux of the chemical reaction, are both less than the CT flux of outwardly migrating reduced porphyrin sites, i.e., $D_{ct}C_{TPP} \gg D_{S,pol}PC_S$ and $D_{ct}C_{TPP}/d \gg k_{ch}IC_S$, the above behavior of the Koutecky-Levich $1/\omega^{1/2} = 0$ intercepts is understandable in that equation 11 reduces to the simple, chemical reaction controlled intercept

of equation 6, in which Panel A of Figure 4 represents the electrocatalytic reaction profile. In this picture, only the porphyrin sites in the outermost boundary of the film are catalytically operative, and increases in Γ_T beyond completion of this boundary amount of porphyrin yield no dividend in increased catalytic rate.

According to this interpretation, the fold-over coverage in the data of Figure 7 measures the quantity of porphyrin sites present in the outermost boundary or catalytically active zone of the film i.e., ca. 1×10^{-10} mole/cm.². This value is close to that estimated, 1.2×10^{-10} mole/cm.², for a coplanar monomolecular level of tetra(p-aminophenyl)porphyrin attached to Pt^{14a}, which implies then that the catalytically active zone is approximately one monomolecular layer thick.

The following support the above interpretation. The coverages Γ_T on Pt/ $\sim$ (Cu)(NH₂)₄TPP electrodes in Table II all exceed monomolecular levels and so the constancy of $k_{ch}\Gamma$ values there is consistent with and expected from the above interpretation. Secondly, in Figure 1, comparison of Curves E and F near the foot of the wave shows that current for PhCHBrCH₂Br reduction is depressed at a potential positive of the electrocatalytic wave on a modified surface, supporting the picture of low PhCHBrCH₂Br flux through the film once porphyrin is bound to it. Thirdly, we observe much lower catalytic rates on Pt/ $\sim$ (Co)(NH₂)₄TPP surfaces which are not exhaustively metallated. The free base (NH₂)₄TPP sites on such electrodes, being catalytically unstable, become silent, and appear to dilute the active Co(NH₂)₄TPP sites and impede substrate access to them. An example is shown in Figure 8, where by comparison of Curves A and B only ca. 50% of the original sites are metallated, and although Γ_T for Co(NH₂)₄TPP sites is high (3.2×10^{-10} mole/cm.²), a submonomolecular rate, $k_{ch}\Gamma = 0.002$

cm./sec., is observed. Finally, that charge transport through the film is fast compared to the catalytic rate was directly demonstrated by potential step chronoamperometry²⁹ of a 1.2×10^{-9} mole/cm.² Pt/ $\sim$ (NH₂)₄-TPP electrode, following our previously described approach to measuring D_{ct} ²⁰. The film charged very rapidly, >95% in 10 msec., and using $C_{TPP} = 2 \times 10^{-3}$ mole/cm.³, only a lower limit for D_{ct} (4×10^{-11} cm.²/sec.) could be estimated. A film with $\Gamma_T = 2 \times 10^{-9}$ mole/cm.² ($d \sim 10$ nm) and this D_{ct} should support a CHEM flux of ca. 8×10^{-8} eqvs/cm.²sec. or a current of 8 ma./cm.², which is much larger than the catalytic currents measured in these experiments.

For electrocatalysis by a polymer film with control by the rate of the chemical step, whether the quantity of catalyst sites corresponds to the outermost layer of the film, or to that in the total film (Γ_T), is predicted by Panels A and B of Figure 4 to depend on the ordering of CHEM flux, CT flux, and SUBS flux. In the electrocatalytic reduction of PhCHBrCH₂Br by Pt/ $\sim$ (Cu)(NH₂)₄TPP and Pt/ $\sim$ (Co)(NH₂)₄TPP described above, and possibly in the results of Oyama and Anson^{6a}, it appears that the quantity of catalyst sites is monolayer-like, corresponding to Panel A, Figure 4. In the electrocatalytic results of Lewis, et al^{5a}, on the other hand, using a small substrate (iodide) which should be partitioned into the cationic polymer, SUBS flux is apparently larger and the result is closer to Panel B, Figure 4.

Using a single rotated disk Pt/ $\sim$ (Co)(NH₂)₄TPP electrode to facilitate comparison of kinetics, i_{max} for reduction of PhCHBrCH₂Br, PhCHBrCHBrPh, and CH₂BrCHBrCH₃ were determined as a function of ω , giving Koutecky-Levich plots comparable to Figure 6, and results for $k_{ch} \Gamma$ which

are shown in Table III. $k_{ch}\Gamma$ was not determined as a function of Γ_T for PhCHBrCHBrPh and $\text{CH}_2\text{BrCHBrCH}_3$, so whether the catalytically active zone of a $\text{Pt}/\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$ electrode is the same for these substrates as for $\text{PhCHBrCH}_2\text{Br}$ (e.g., $1 \times 10^{-10} \text{ mole/cm}^2$) is uncertain. Assuming³⁰ that it is, we have converted the $k_{ch}\Gamma$ values for these substrates to k_{ch} by dividing the monolayer value $\Gamma = 1 \times 10^{-10} \text{ mole/cm}^2$. Results of Figure 7 and for $\text{Pt}/\text{m}(\text{Cu})(\text{NH}_2)_4\text{TPP}$ in Table II, converted to k_{ch} on the same basis, are also given in Table III, to facilitate their comparison. Values of $k_{ch}\Gamma$ where $\Gamma < 1 \times 10^{-10} \text{ mole/cm}^2$ in Figure 7 are divided by the actual Γ since complete access is indicated in those cases.

Andrieux, et al.³¹ have shown in the homogeneous electrocatalytic reductions of monohaloaromatics with aromatic radical anions, that the RDS involves formation of an $\text{ArX}^{\cdot-}$ species, that the kinetics slow monotonically in Marcusian fashion as the outer sphere catalyst couple's E° become more positive relative to the $E_{1/2}$ of the ArX reduction wave, and that E° for the $\text{ArX}/\text{ArX}^{\cdot-}$ wave is rather close to the irreversible $E_{1/2}$. If the same principles hold for the present case, the catalytic reduction k_{ch} of $\text{PhCHBrCH}_2\text{Br}$ and $\text{CH}_2\text{BrCHBrCH}_3$ by a $\text{Pt}/\text{m}(\text{Cu})(\text{NH}_2)_4\text{TPP}$ surface should be faster than on $\text{Pt}/\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$, and with $\text{Pt}/\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$ the order in substrate reduction rate should be $\text{PhCHBrCHBrPh} > \text{CH}_2\text{-}$

BrCHBrCH_3 . Only the final one of these anticipations (slow reduction of $\text{CH}_2\text{BrCHBrCH}_3$ by the $\text{Pt}/\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$) is actually observed. Catalytic reduction by $\text{Pt}/\text{m}(\text{Co})(\text{NH}_2)_4\text{TPP}$ is elsewhere faster than expected in comparison with other metalloporphyrins, and the rate order for PhCHBrCHBrPh and $\text{PhCHBrCH}_2\text{Br}$ is the reverse of that expected from outer sphere E° considerations. The conclusion seems obvious that reductions

of these substrates with $(\text{Co}^{\text{I}})(\text{NH}_2)_4\text{TPP}$ sites do not proceed by an outer sphere electron transfer pathway and their behavior is not in conflict with the predictions of Andrieux and Saveant²⁶ as regards outer sphere electrocatalysis by electrodes with monolayer coverages of catalyst. The reaction must involve adduct formation of some sort, but we have no reasonable basis on which to conjecture about the nature of this binding or the mechanistic details of electron transfer. We should take note, however, of the similarity of the rate for the cobalt and copper porphyrin reactions with $\text{PhCHBrCH}_2\text{Br}$ - which may not be fortuitous - and of the greater steric bulkiness of the slower reacting PhCHBrCHBrPh as compared to $\text{PhCHBrCH}_2\text{Br}$. These facts suggest that the RDS in the reaction could involve steric requirements of adduct formation in the poorly penetrable, catalytically active reaction zone of the porphyrin film.

We consider finally use of the rising portion of the catalytic wave for kinetic measurements. Current-potential curves are shown in Figure 9, Curves A,B, for the reduction of $\text{PhCHBrCH}_2\text{Br}$ by a $\text{Pt}/\sim(\text{Cu})(\text{NH}_2)_4\text{TPP}$ electrode (Entry 5, Table II). The half-wave potential, $E_{1/2}$ (at $i = 0.5 i_{\text{max}}$) becomes more positive, at lower electrode rotation rate, as expected from equation 13. Application of equation 13 to calculation of k_{ch}^{I} , however, yields a value of 0.11 cm./sec., in poor agreement with results from i_{max} data and Koutecky-Levich plots (Table II). Further, when the catalytic waveshape is analyzed by equation 13, plotting potential vs. $\log [(i_{\text{max}} - i)/i]$, the plots (Curves D,E) are linear in their central portions but have slopes of 93 mv. rather than the 59 mv. value expected from equation 13. Equation 13 is thus not a good representation of the rising part of the catalytic wave.

The problem with equation 13 is traceable to the assumption in equation 12, that the activity coefficients of oxidized and reduced porphyrin sites are equal and coverage-independent. Electrochemical waves of surface immobilized chemicals in fact show substantial activity effects as pointed out by Brown and Anson and verified elsewhere^{1,14b,32}. The surface wave for Pt/m(Cu)(NH₂)₄TPP has for example $E_{FWHM} = 145$ mv. compared to the 91 mv expected from equation 12. Further, if a plot is made of equation 12 for the Pt/m(Cu)(NH₂)₄TPP surface wave (no substrate, Figure 9, curve F), it has the same high slope (89 mv) as the analogous waveshape plot of equation 13 (Figure 9B, curve C). Equation 13 fails then, because of neglect of an activity problem.

The activity problem can be circumvented by recognizing that, at any given potential, we can write

$$\frac{i_T - i'}{i'} = \left[1 + \frac{k_{ch} i'}{0.62 D_S^{2/3} \nu^{-1/6} \omega^{1/2}} \right] \left[\frac{i_{max} - i}{i} \right] \quad (14)$$

The left-hand side of equation 14 can be evaluated from the Pt/m(Cu)(NH₂)₄TPP surface wave so as to explicitly represent the porphyrin activity. If $k_{ch} i'$

is evaluated from equation 14, and accounting for the electron stoichiometry of equation 5, a value of 0.019 cm./sec. results from Figure 9, in much better agreement with the Koutecky-Levich result.

A similar analysis of the rising part of the catalysis for $\text{PhCHBrCH}_2\text{Br}$ at a $\text{Pt}/\text{Co}(\text{NH}_2)_4\text{TPP}$ electrode produced via equation 14 a $k_{\text{ch}}\Gamma'$ of 0.015 cm./sec. as compared to 0.015 for the Koutecky-Levich plot for this electrode. Nonetheless, the rising part of the current potential curve seems less promising for kinetic measurements than the use of equation 6.

Chronoamperometry. Potential step chronoamperometry has not previously been applied to the study of modified electrode electrocatalysis. Its theory is straightforward. Solution of Fick's laws for substrate S under the boundary conditions $D_S(dC_S/dx)_{x=0} = (d\Gamma/dt) = k_{\text{ch}}\Gamma'_R C_S$ yields the current-time equation

$$i = nFAk_{\text{ch}}\Gamma'_R C_S \exp \left[\frac{k_{\text{ch}}\Gamma'_R t^{1/2}}{D_S^{1/2}} \right]^2 \text{erfc} \left[\frac{k_{\text{ch}}\Gamma'_R t^{1/2}}{D_S^{1/2}} \right] \quad (15)$$

where $\Gamma'_R = \Gamma$ if the potential step is well onto the plateau of the catalytic wave and $\Gamma'_R = \Gamma/(1 + \exp[\frac{nF}{RT}(E_{\text{surf}}^\circ - E)])$ if onto the rising portion of the wave. Equation 15 is of the same form as the known relationship for slow charge transfer at naked electrodes³³ where the heterogeneous electron transfer rate constant $k_{f,h}$ is identified with $k_{\text{ch}}\Gamma'$. The essential difference between the older theory and that for modified electrode electrocatalysis is that $k_{f,h}$ increases exponentially with potential (and so there is no wave plateau unless mass transfer intervenes) whereas $k_{\text{ch}}\Gamma'_R$ increases with potential only to a maximum value of $k_{\text{ch}}\Gamma$. The current-time form of equa-

tion 15 can be inspected in several ways;²⁷ we elected to use plots of i vs. $t^{-1/2}$, a form to which equation 15 linearizes at long time in the experiment, when current becomes limited by the rate of substrate diffusion rather than by the rate of the catalytic reaction.

The chronoamperometric experiment was applied to reduction of PhCHBrCHBrPh with Pt/ ω (Co)(III₂)₄TPP electrodes for which the value of $k_{ch}\Gamma$ had been first determined from rotated disk electrode data via a Koutecky-Levich plot. Figure 10A shows such a plot for PhCHBrCHBrPh reduction and Figure 10B shows the current-time curves for a potential step to -1.0 volt vs. SSCE at this electrode in a quiet solution of 1.2 mM PhCHBrCHBrPh and in a solution containing no substrate (for background current correction). Figure 11 shows that the current time response is accurately fit by equation 15 using a value of $k_{ch}\Gamma = 1.66 \times 10^{-3}$ cm./sec. (the same as obtained from the rotated disk experiment) and a value of $D_S = 2.65 \times 10^{-6}$ cm.²/sec obtained by a direct potential step reduction (at -1.65 volt) of PhCHBrCHBrPh at a naked Pt electrode. A similarly good comparison was obtained in an experiment with a different electrode and 5mM substrate. The chronoamperometric experiment is simple to apply and this comparison shows that it can be an accurate technique for electrocatalytic measurements. We should note, however, that equation 15 assumes (as does equation 6) fast charge transport through the catalyst film, which may not be the case with other catalyst film systems. Additionally, inclusion of theory for charge transport and substrate diffusion rate effects is a more complex problem than in rotated disk electrode voltammetry, owing to the steady state character of the latter.

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TABLE I

Cyclic Voltammetric Estimates^b of Alkyl Dibromide Electrocatalysis in DMSO

Porphyrin ^a , E_{surf}°	Substrate, $E_{\text{p,uncat.}}$		
	ØCHBrCHBrØ , -1.32	$\text{ØCHBrCH}_2\text{Br}$, -1.40	$\text{CH}_3\text{CHBrCH}_2\text{Br}$, -1.89
Mn, -0.30	no	no	no
Co, -0.87	fast	fast	slow
Free base, -1.12	fast ^c	fast ^c	no
Cu, -1.21	d	fast	no
Zn, -1.42	d	d	no

^a Immobilized on glassy carbon electrode by Reaction 2. Potentials referenced to NaCl saturated SCE.

^b "Fast" means approximately diffusion controlled.

^c Reacts with substrate.

^d Excessive overlap with the uncatalyzed reduction.

TABLE II

Electrocatalysis Kinetics^a from Rotated Disk Voltammetry.Reduction of $\text{PhCHBrCH}_2\text{Br}$ by $\text{Pt}/\sim(\text{Cu})(\text{NH}_2)_4\text{TPP}$ in DMSO.

Entry	$T, ^\circ\text{C}$	$\Gamma_T, \text{mole/cm}^2$	C_S, mM	$k_{\text{ch}}\Gamma, \text{cm/sec}$
1	20	4.1×10^{-10}	0.69	.0089
2	20	5.9×10^{-10}	1.16	.010
3	20	19×10^{-10}	0.49	.0094
4	25	2.3×10^{-10}	0.62	.011
5	25	5.8×10^{-10}	0.68	.011
6	25	8.3×10^{-10}	0.48	.014
7	25	10.5×10^{-10}	0.66	.013
8	30	5.9×10^{-10}	1.16	.015
9	40	5.9×10^{-10}	1.16	.019
10	50	5.9×10^{-10}	1.16	.024

^a A value of $n=2$ is used in calculation of these data from equation 6, considering the electron stoichiometry of Reaction 4.

TABLE III

Rotated Disk Electrode Voltammetry Kinetic Results
For Electrocatalytic Reductions at 20°C in 0.1 M Et₄NClO₄ in DMSO

Substrate Pt/ $\sim$ (Co)(NH ₂) ₄ TPP (E°= -0.86)	E _{1/2} ^{direct} v. vs. SSCE	Γ_T , mole/cm ²	C _S , mM	k _{ch} Γ , cm/sec	k _{ch} , l/mole-sec
PhCHBrCHBrPh	-1.36	2.5x10 ⁻¹⁰	1.0	4.0x10 ⁻³	4.0x10 ⁴ a
PhCHBrCH ₂ Br	-1.45	2.5x10 ⁻¹⁰	1.0	1.4x10 ⁻²	1.4x10 ⁵ a
CH ₂ BrCHBrCH ₃	-1.89	2.5x10 ⁻¹⁰	4.0	1.5x10 ⁻⁴	1.5x10 ³ a
PhCHBrCH ₂ Br ^b	-1.45	0.29x10 ⁻¹⁰		2.9x10 ⁻³	1.0x10 ⁵
		0.58x10 ⁻¹⁰		5.0x10 ⁻³	0.9x10 ⁵
		0.71x10 ⁻¹⁰		9.4x10 ⁻³	1.3x10 ⁵
		2.1x10 ⁻¹⁰		1.0x10 ⁻²	1.0x10 ⁵ a
		3.8x10 ⁻¹⁰		9.3x10 ⁻³	0.9x10 ⁵ a
Pt/ $\sim$ (Cu)(NH ₂) ₄ TPP (E°= -1.23)					
PhCHBrCH ₂ Br ^c	-1.45	4.1-19x10 ⁻¹⁰		9.4x10 ⁻³	0.9x10 ⁵ a

^a Calculated on basis of active $\Gamma = 1 \times 10^{-10}$ mole/cm².

^b Data from Figure 7 at 75° metallation.

^c Data at 20° from Table II, averaged.

FIGURE LEGENDS

Figure 1. Cyclic Voltammetry.

Panel A: Electrocatalytic reduction of 1 mM PhCHBrCH₂Br by C/-(Co)(NH₂)₄TPP in DMSO/0.1 M TEAP, 100 mV/sec, SSCE reference, 25°C; curve A, porphyrin surface, no substrate, $\Gamma_T = 4.2 \times 10^{-10}$ mole/cm²; curve B, catalyzed reduction; curve C reduction of substrate on naked glassy carbon. $E_{p,uncat.} = -1.40$ volts.

Panel B: Electrocatalytic reduction of 2.62 mM PhCHBrCH₂Br by Pt/-(Co)(NH₂)₄TPP in DMSO/0.1 M TEAP, 100 mV/sec, SSCE reference, 25°C; curve D, porphyrin surface, $\Gamma_T = 5.45 \times 10^{-10}$ mole/cm²; curve E, catalyzed reduction; curve F, reduction of substrate on naked Pt electrode, $E_{p,uncat.} = -1.44$ volts. Comparison of the foot of curves E and F shows that direct substrate reduction at the modified electrode is blocked by the catalyst film.

Figure 2. Cyclic voltammetry of 1 mM PhCHBrCHBrPh at C/-(M)(NH₂)₄TPP in DMSO/0.1 M TEAP, 100 mV/sec, SSCE reference, 25°C. $\Gamma_T(Mn) = 1.7 \times 10^{-10}$ mole/cm², $\Gamma_T(Co) = 2.5 \times 10^{-10}$, $\Gamma_T(NH_2)_4TPP$ (Free Base) = 3.9×10^{-10} , all curves except "blank C" contain both substrate and porphyrin layer.

Figure 3. Cyclic voltammetry of 1 mM CH₃BrCH₂Br at C/-(M)(NH₂)₄TPP in DMSO/0.1 M TEAP, 100 mV/sec, SSCE reference, 25°C, $\Gamma_T(Mn) = 1.7 \times 10^{-10}$ mole/cm², $\Gamma_T(Co) = 2.5 \times 10^{-10}$, Γ_T (Free Base) = 1.0×10^{-10} , $\Gamma_T(Zn) = 8 \times 10^{-11}$, all curves except "blank C" contain both substrate and porphyrin layer.

Figure 4. Estimated steady state concentration distance profiles of catalyst sites (CAT ●●●) and substrate (SUBS —) for electrocatalysis at rotated disk electrode, at the $1/\omega^{1/2}$ intercept of a

$1/i_{\max}$ vs. $1/\omega^{1/2}$ plot, assuming $C_S = 1 \times 10^{-6}$ mole/cm.³, $\Gamma_T = 1 \times 10^{-9}$ mole/cm.², $d = 1 \times 10^{-6}$ cm., $C_{\text{TPP}}(x=0) = 1 \times 10^{-3}$ mole/cm.³, flux values all in mole/cm.²sec. PANEL A: $(\text{CHEM flux})_{\lim} = 1 \times 10^{-8}$ mole/cm.²sec., $\text{CT flux} = 4 \times 10^{-7}$ ($D_{\text{ct}} = 4 \times 10^{-10}$ cm.²/sec.), $\text{SUBS flux} = 1 \times 10^{-9}$ ($D_{\text{S,pol}}^{\text{P}} = 1 \times 10^{-9}$ cm.²/sec.), $k_{\text{ch}} \Gamma C_S = 1 \times 10^{-8}$; PANEL B: $(\text{CHEM flux})_{\lim} = 1 \times 10^{-8}$ mole/cm.²sec., $\text{CT flux} = 4 \times 10^{-7}$ ($D_{\text{ct}} = 4 \times 10^{-10}$ cm.²/sec.), $\text{SUBS flux} = 1 \times 10^{-6}$ ($D_{\text{S,pol}}^{\text{P}} = 1 \times 10^{-6}$ cm.²/sec.), $k_{\text{ch}} \Gamma C_S = 1 \times 10^{-8}$; PANEL C: $(\text{CT flux})_{\lim} = 4 \times 10^{-7}$ mole/cm.²sec ($D_{\text{ct}} = 4 \times 10^{-10}$ cm.²/sec.), $\text{CHEM flux} > 4 \times 10^{-6}$ (●●●), 4×10^{-5} (●●●), $\text{SUBS flux} = 1 \times 10^{-9}$ ($D_{\text{S,pol}}^{\text{P}} = 1 \times 10^{-9}$ cm.²/sec.); PANEL D: $(\text{SUBS flux})_{\lim} = 1 \times 10^{-8}$ ($D_{\text{S,pol}}^{\text{P}} = 1 \times 10^{-8}$ cm.²/sec., $q = 1 \times 10^{-7}$ cm.), $\text{CHEM flux} = 1 \times 10^{-4}$ ($C_{\text{TPP}}(x=10^{-7}) = 0.01 C_{\text{TPP}}(x=0)$; $C_S(x=10^{-7}) = 0.01 C_S(x=d)$), $\text{CT flux} = 1 \times 10^{-9}$ ($D_{\text{ct}} = 1 \times 10^{-12}$ cm.²/sec., $p = 1 \times 10^{-7}$ cm.).

Figure 5. Rotated disk voltammetry for the reduction of 0.69 mM PhCHBrCH₂Br at a Pt/-(Cu)(NH₂)₄TPP electrode ($\Gamma_T = 4.1 \times 10^{-10}$ mole/cm.²), DMSO/0.1 M TEAP, SSCE reference, 10 mV/sec sweep rate, 20°C. This electrode is entry 1 in Table II.

Figure 6. Plot of $i_{\max}^{-1}$ versus $\omega^{-1/2}$ according to equation 6 for data of Figure 5 (Entry 1, Table II) and of Entries 2,3, Table II. The intercepts are inversely proportional to the concentration of PhCHBrCH₂Br (see $k_{\text{ch}} \Gamma$ in Table II). The slopes are also inversely proportional to concentration; the ratio of slope to C_S for the curves A,B,C is 4.9, 5.5, 5.4 .

Figure 7. $k_{ch}\Gamma$ vs. Γ for the reduction of 1 mM PhCBrCH₂Br at Pt/ $\sim$ (Co)(NH₂)₄TPP electrodes. DMSO/0.1 M TEAP, 20°C. For each electrode, cobalt was inserted by warming the porphyrin modified electrode to 75°C (●) or 90°C (□) for 6 hours in a $\sim$ 1 M solution of CoCl₂ in DMF. Complete metallation was confirmed by comparing Γ_T measured before and after metal insertion.

Figure 8. Cyclic voltammetry of Pt/ $\sim$ (Co)(NH₂)₄TPP after (Curve A) and before (Curve B) metallation, in the absence of substrate, in DMSO/0.1 M TEAP, $v = 100$ mV/sec, SSCE reference. Γ_T (Free Base) = 5.75×10^{-10} mole/cm², Γ_T (Co) = 3.2×10^{-10} , indicating incomplete metallation. Curve C: Koutecky-Levich plot for this electrode in 1 mM PhCHBrCH₂Br, 20°C. From intercept, $k_{ch}\Gamma = 2 \times 10^{-3}$ cm/sec.

Figure 9. Curves A, B: Rotated disk voltammetry for the reduction of 0.68 mM PhCHBrCH₂Br by a Pt/ $\sim$ (Cu)(NH₂)₄TPP electrode, sweep rate = 10 mV/sec; Curve C: porphyrin electrode without substrate present, showing only cathodic voltammogram, $\Gamma_T = 5.8 \times 10^{-10}$ mole/cm², 100 mV/sec; Curves D, E: plots of Curves A and B according to equation 13; Curve F: plot of Curve C according to equation 12.

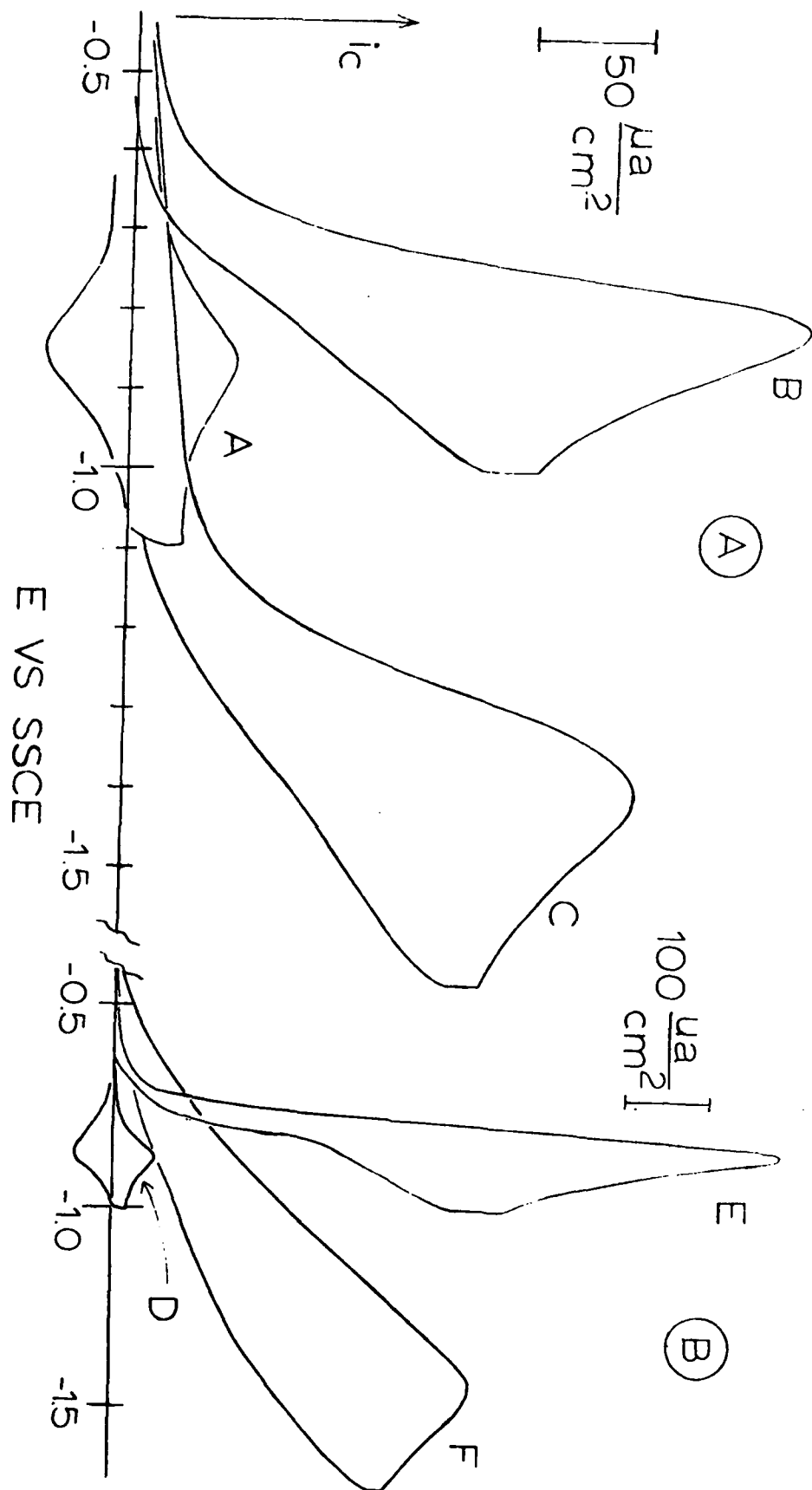
Figure 10.

Panel A: $1/i_{max}$ vs. $1/\omega^{1/2}$ from rotated disk reduction of 1.17 mM PhCHBrCHBrPh at a Pt/ $\sim$ (Co)(NH₂)₄TPP electrode, $\Gamma_T = 3.3 \times 10^{-10}$ mole/cm² in DMSO/0.1 M TEAP, 25°C.

Figure 10, continued:

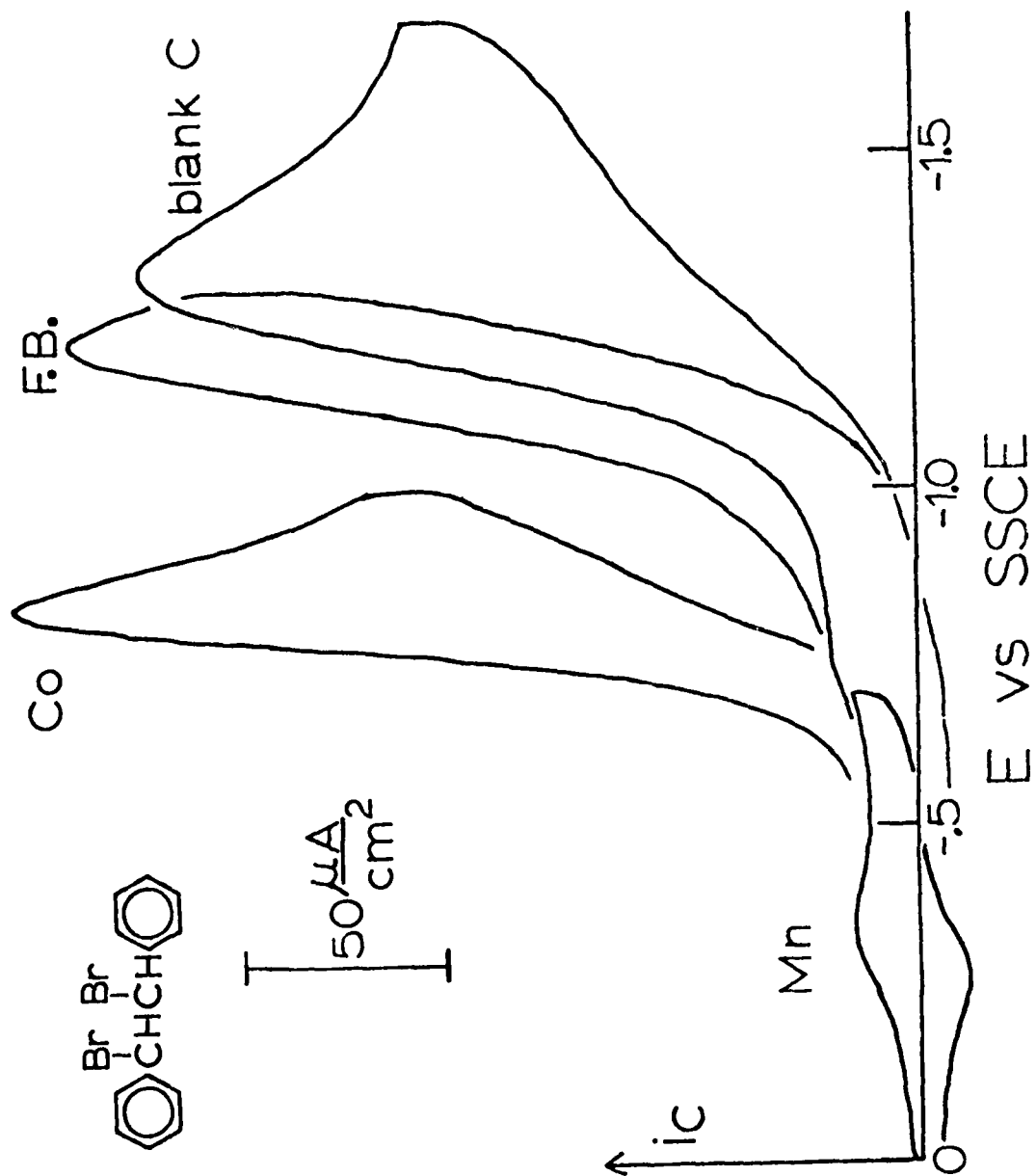
Panel B: Chronoamperometric current time curves at the same electrode in 1.17 mM PhCHBrCHBrPh for a potential step from -0.6 volts to -1.0 volts vs. SSCE reference. The solid line is the catalytic reduction, (---) is the uncatalyzed reduction, and (----) is a potential step with the modified electrode in a solution containing no substrate.

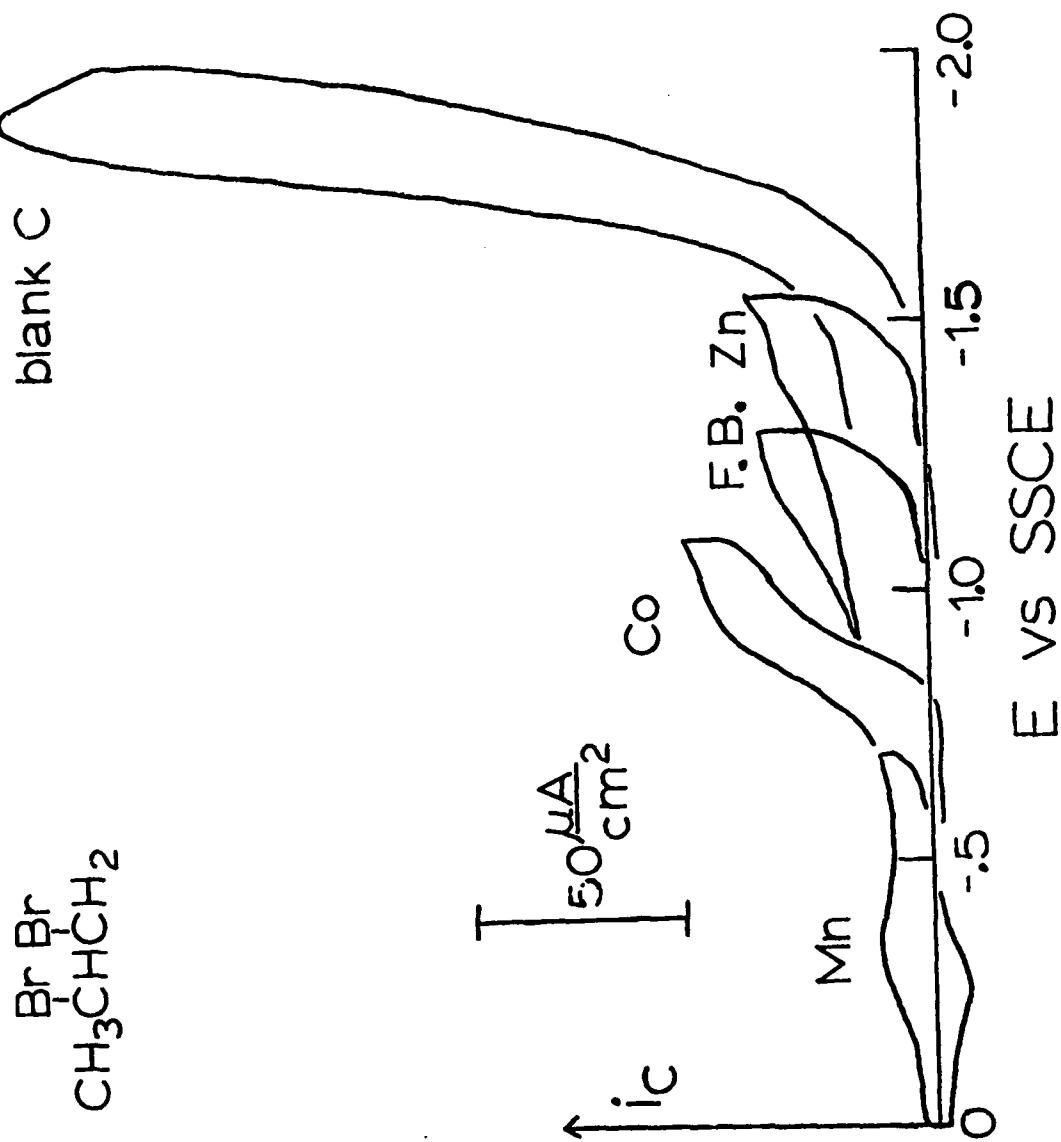
Figure 11. i vs. $t^{-1/2}$ (solid curve) from the data of Figure 10B plus other data taken at short time (0 to 0.37 sec.). The currents are corrected for the background current from a potential step with a modified electrode in a solution containing no substrate. From Figure 10A, $k_{ch}\Gamma = 1.66 \times 10^{-3}$ cm/sec. for this electrode. Points (●) represent theoretical prediction of equation 15 for $k_{ch}\Gamma = 1.66 \times 10^{-3}$ cm/sec and $D_S = 2.65 \times 10^{-6}$ cm²/sec. The linear solid line is a Cottrell slope calculated for $D_S = 2.65 \times 10^{-6}$ cm²/sec.



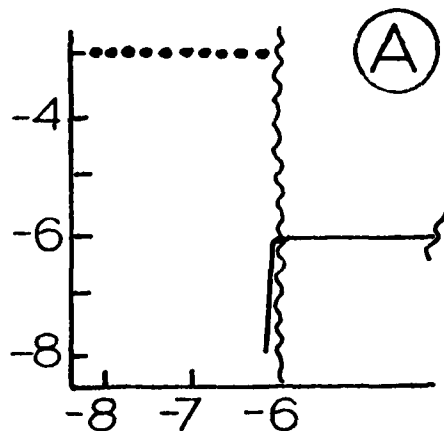
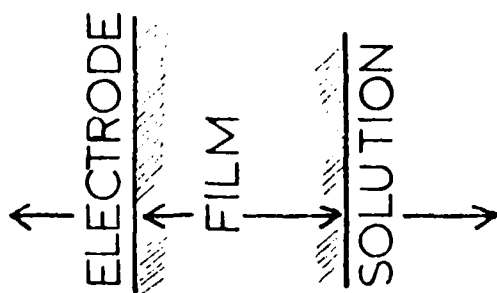
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Fig 1

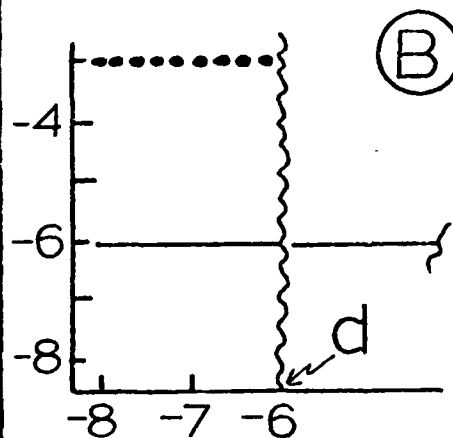




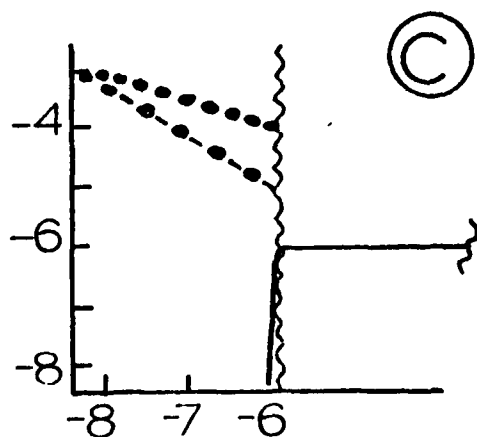
$\frac{\text{mole}}{\text{cm}^3}$
 catalyst sites...
 log(conc. substrate—
 substrate—



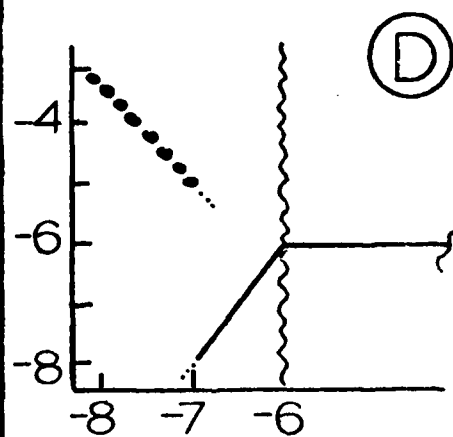
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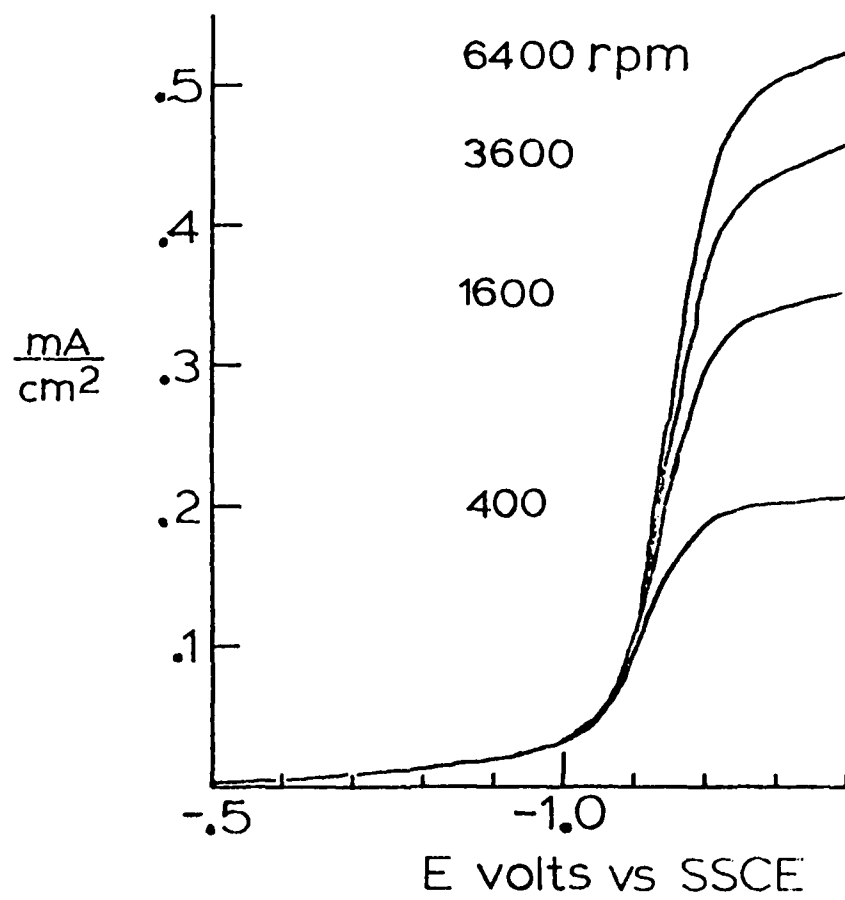


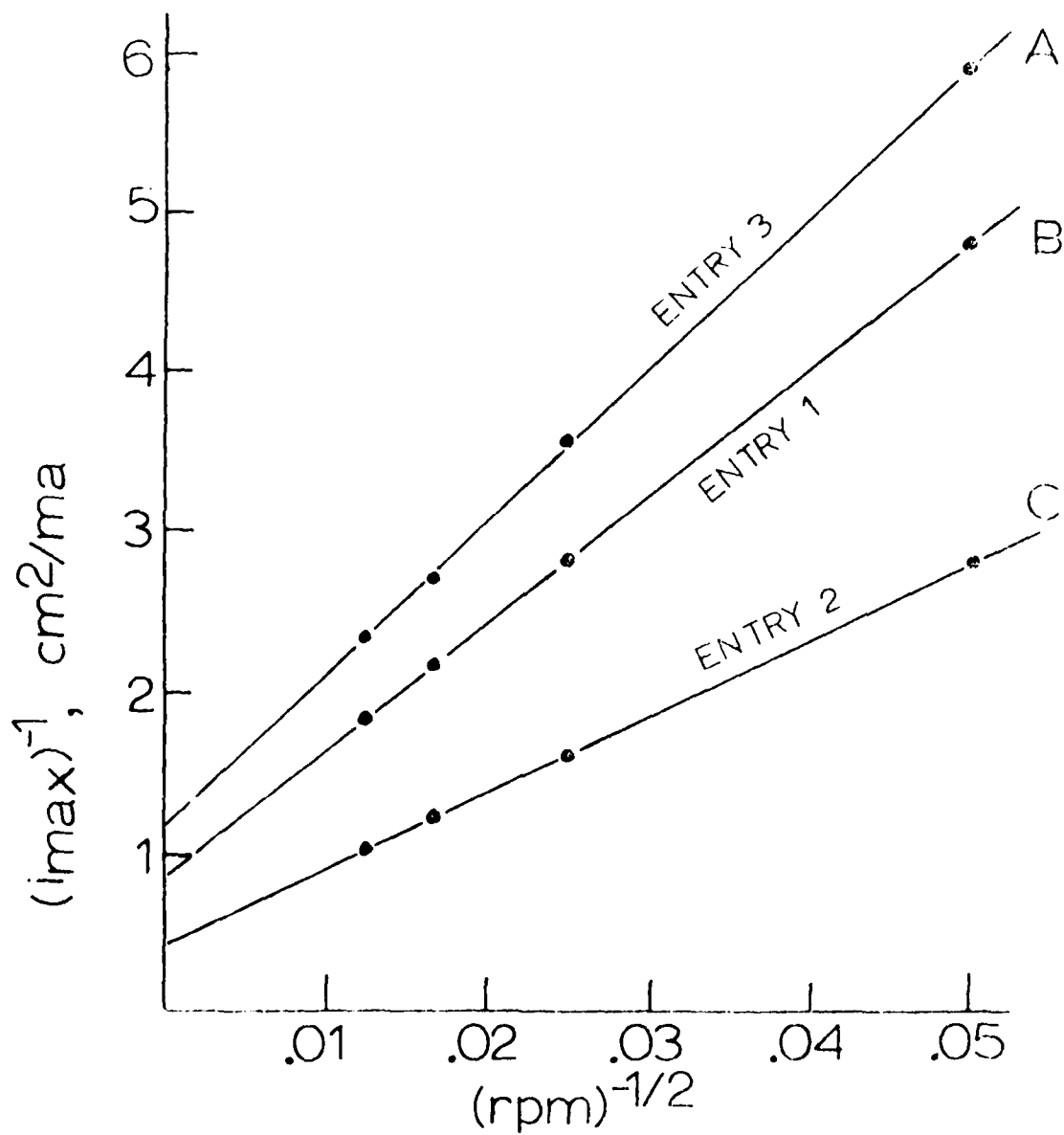
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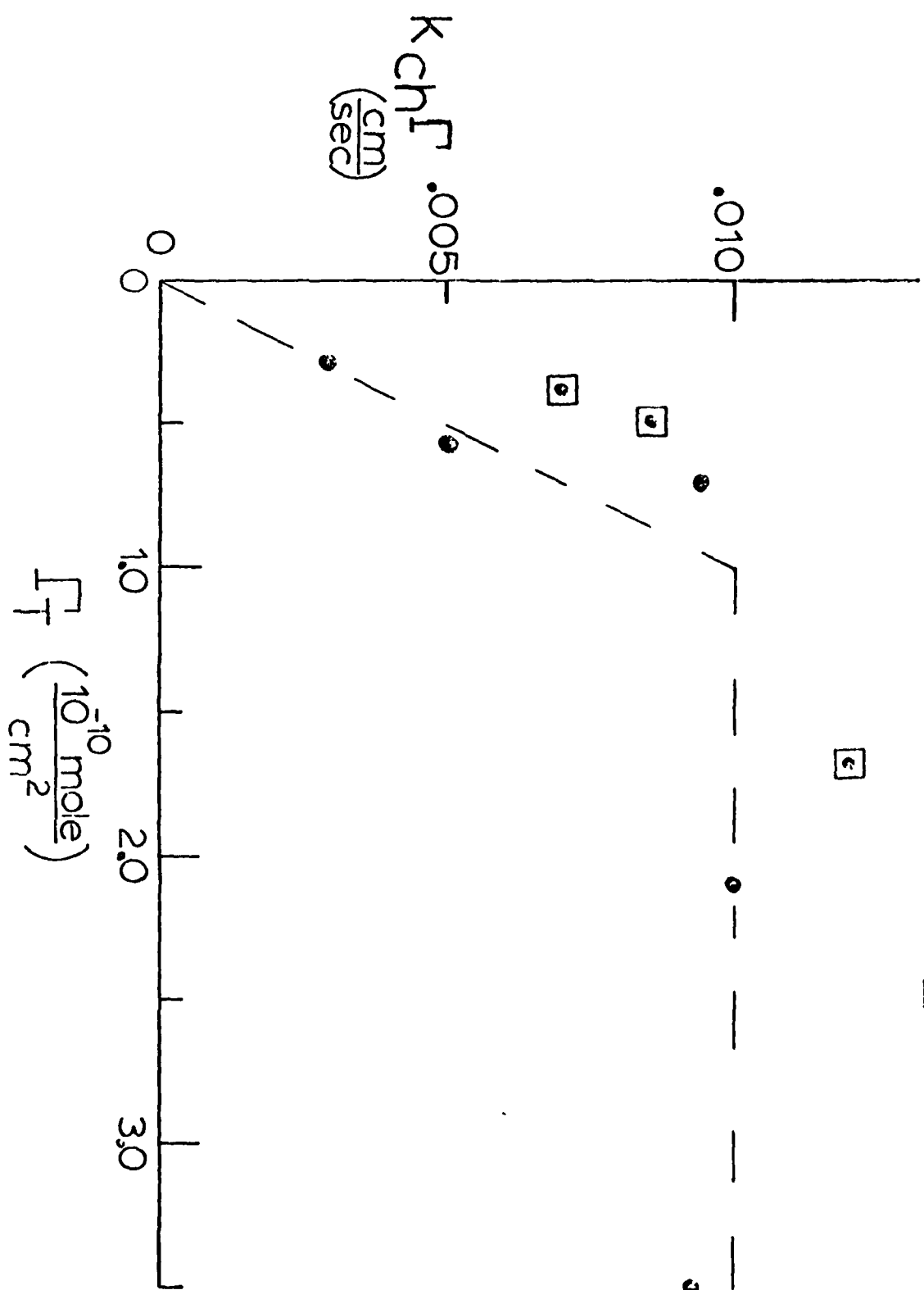


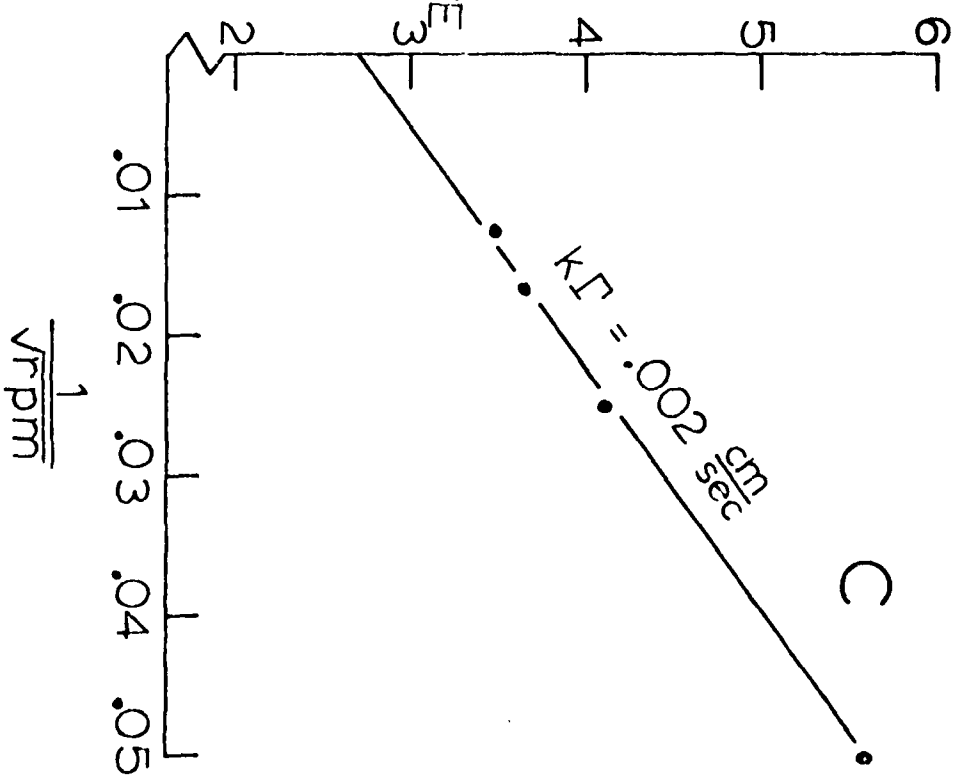
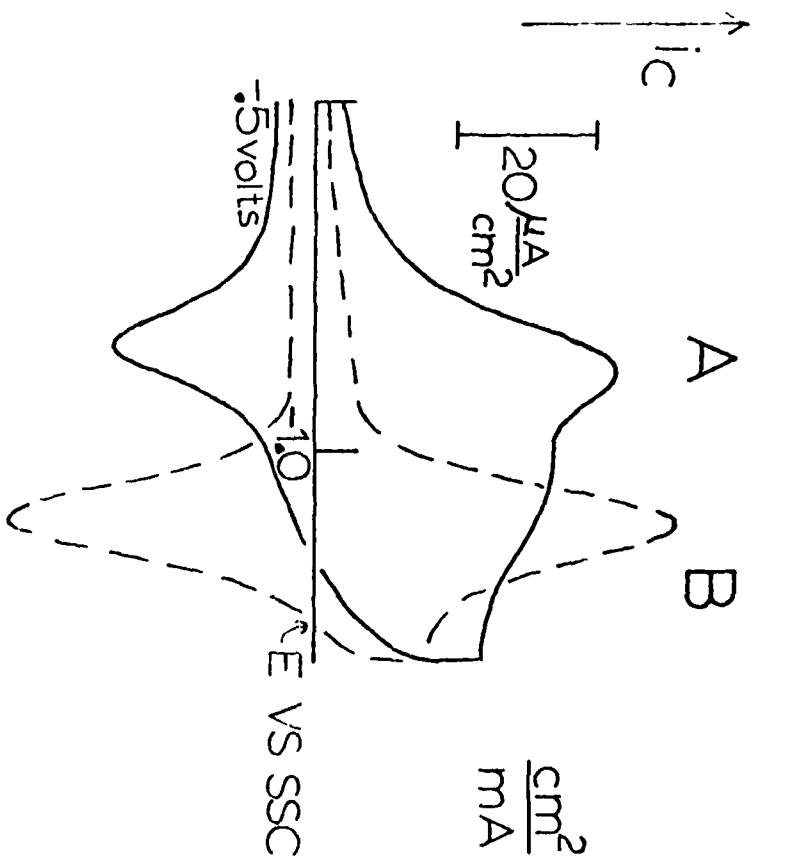
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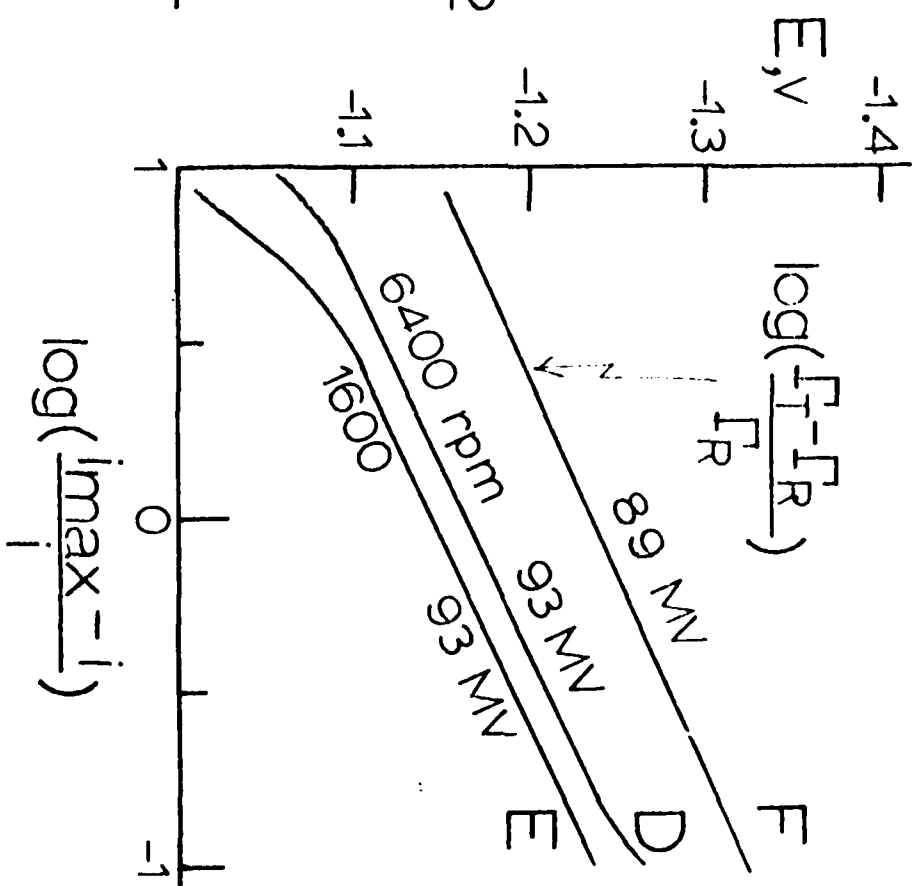
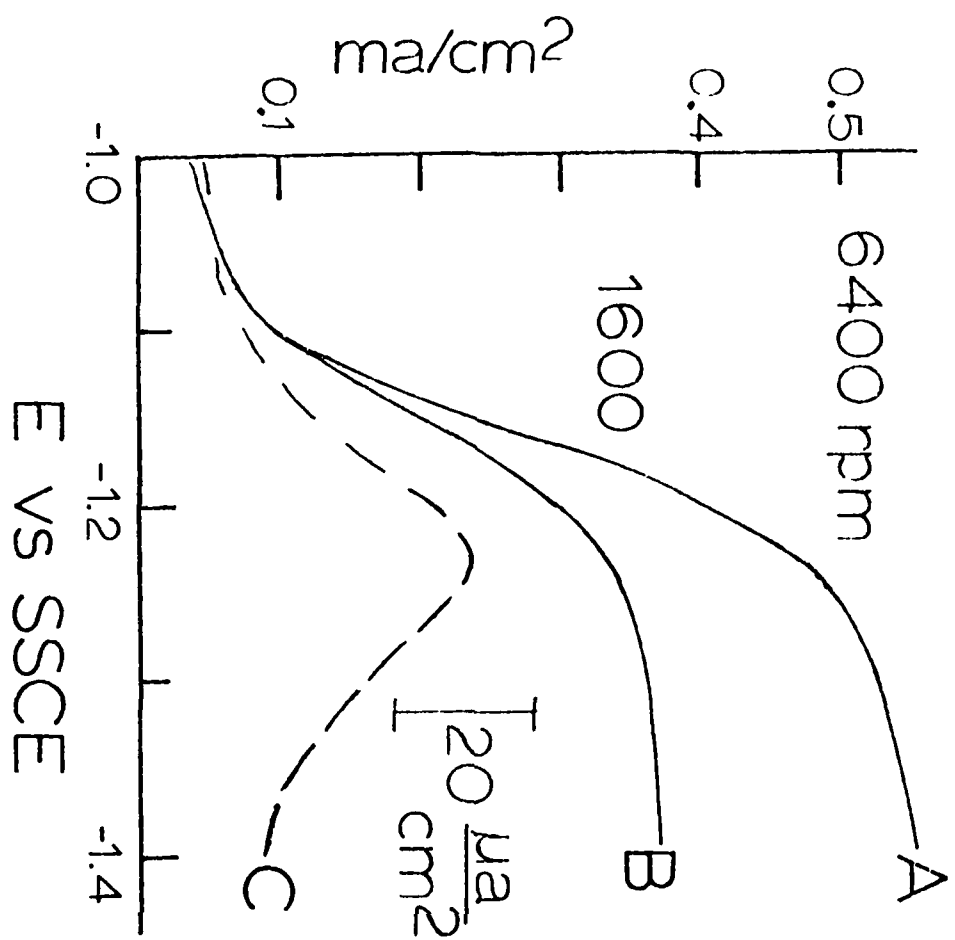
log (distance from electrode)₄

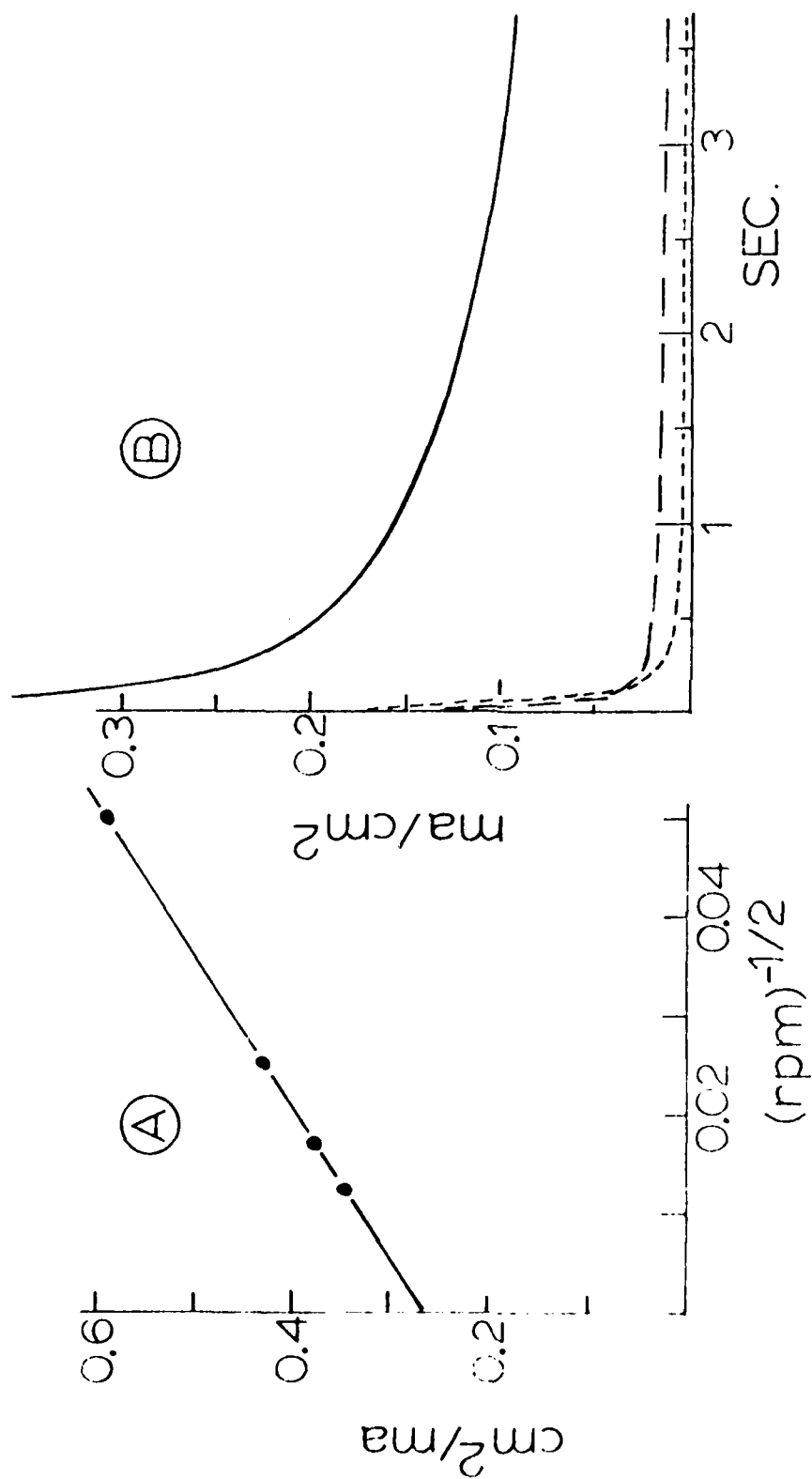


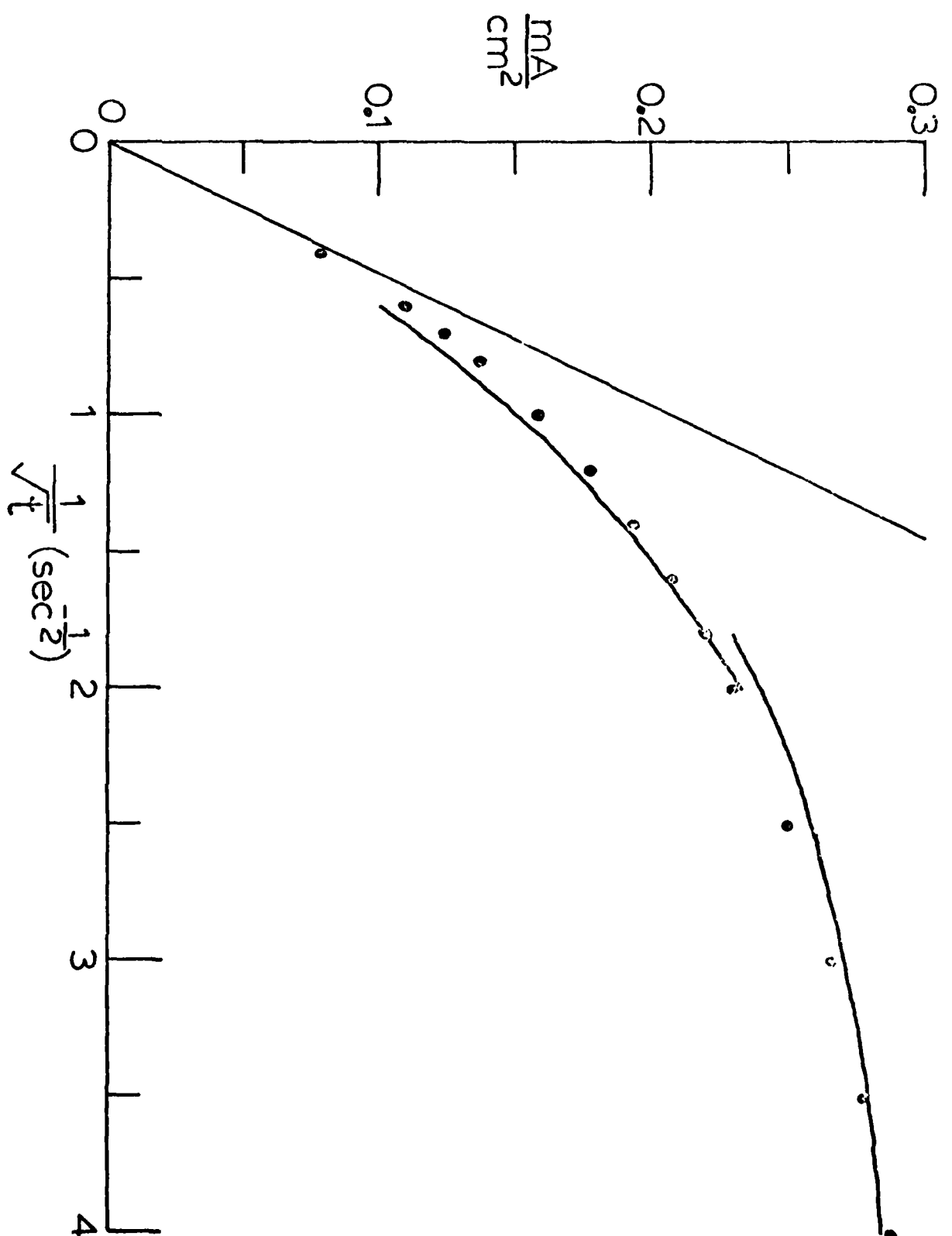












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