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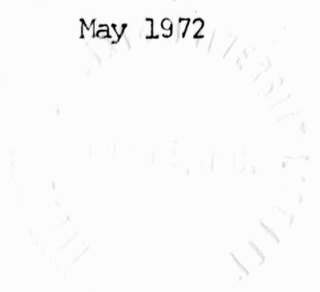
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AN EXPERIMENTAL POLAROGRAPHIC INVESTIGATION OF
SOME TRANS-DICHLOROBIS(SUBSTITUTED ANILINE)PALLADIUM(II)
COMPOUNDS IN N,N-DIMETHYLFORMAMIDE

A Thesis
Presented to
The Faculty of the Department of Chemistry
Appalachian State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Arts

by
Lester Wade Chittam
May 1972



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SOME TRANS-DICHLOROBIS(SUBSTITUTED ANILINE)PALLADIUM(II)
COMPOUNDS IN N,N-DIMETHYLFORMAMIDE

by
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Sixteen trans-dichlorobis(substituted aniline)palladium(II) compounds were synthesized. N,N-Dimethylformamide was used as the solvent in preparing solutions of these palladium compounds for polarographic reduction. All solutions were made 10^{-3} M in the palladium compounds and 10^{-1} M in potassium perchlorate, the supporting electrolyte.

Solutions of all sixteen compounds were polarographically reduced at a temperature of $25 \pm 0.2^\circ$. The half-wave potentials, $E_{1/2}$, of these palladium compounds were determined, and shifts in the half-wave potentials were observed. Plots of $E_{1/2}$ versus σ_X , the Hammett substitution parameter, were made. A correlation was found between the shifts in the half-wave potentials and the meta substituents and a possible correlation was found between the shifts in the half-wave potentials and the para substituents.

CHAPTER I

THE PROBLEM AND REVIEW OF LITERATURE

The Problem

The purposes of this study were 1) to obtain the reduction half-wave potentials, $E_{1/2}$, of several trans-dichlorobis(substituted aniline)palladium(II) complexes; 2) to compare these values to that of the parent compound trans-dichlorobis(aniline)palladium(II); 3) to ascertain and measure any shift in the half-wave potential; and 4) determine any correlation between these shifts and Hammett substitution parameter, σ_X , for the substituent.

Review of Literature

Non-aqueous solvents are useful in studying many water-insoluble compounds. N,N-Dimethylformamide, DMF, is one such solvent and its use as a solvent in polarography is relatively new. In November, 1957, G. H. Brown and Rasmia Al-Urfali (1) stated that as far as they had been able to determine there had been only one previous reference to the use of DMF in polarography of inorganic salts. The purpose of their study was to determine the half-wave potentials of some alkali metal ions, alkaline earth metal ions, and some transition metal ions. The supporting electrolyte for the polarographic reduction of the transition metals--cobalt, copper, nickel, and zinc--was 0.2M sodium perchlorate.

Findeis and De Vries used N,N-Dimethylformamide as the solvent in their polarographic reductions of potassium tetraphenylborate(III). The purpose

of their research was to determine if potassium tetrphenylborate(III) could be determined by a polarographic method. Tetrabutylammonium iodide (0.25M) was used as the supporting electrolyte. The wave heights were proportional to concentrations over the range 0.0002 to 0.0075 which corresponds to 0.08 to 3.0 mg. of potassium in the polarographic cell. The half-wave potential was a -1.55 volts with a mercury pool as non-polarized electrode. (3)

A study of the polarographic reduction of some palladium complexes in aqueous solvent was made by J. B. Willis(10). One ml. of an analyzed stock solution of a salt of the metal was added to an excess of a complex-forming substance to prepare the solution. The solutions were 0.001M with respect to the palladium and 1M with respect to the complex-forming substance which was also used as the supporting electrolyte. His study determined the following half-wave potentials expressed relative to the saturated calomel electrode: $[\text{Pd}(\text{CN})_4]^{--}$, -1.77 v.; $[\text{Pd}(\text{NH}_3)_4]^{++}$, -0.734 v.; $[\text{Pdpy}_4]\text{Cl}_2$, -0.321 v.; $[\text{Pden}_2]^{++}$, -0.76 v. An irregular drop rate of the mercury was observed near the top of the curve of $[\text{Pd}(\text{CN})_4]^{--}$ and $[\text{Pden}_2]^{++}$. In comparing the stabilities of palladium(II)-amine complexes, Willis concluded that the more basic the amine the more negative the half-wave potential of the complex.

Zuman studied the reduction of copper from some of its complexes (13). He found a correlation of the half-wave potential of copper to σ_X values.

CHAPTER II

SYNTHESIS OF THE PALLADIUM COMPLEXES

A polarographic study of sixteen palladium complexes was made during the investigation. At the initiation of this research there was no known literature reference to the synthesis for most of these compounds; therefore, an account of the synthesis of each compound follows.

The compounds in general were prepared by adding a solution of the ligand in DMF to a warm hydrochloric acid solution of PdCl_2 according to a common procedure (2). The compounds synthesized for this investigation are listed in Table I.

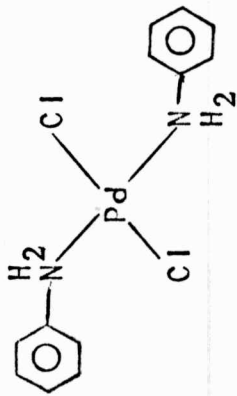
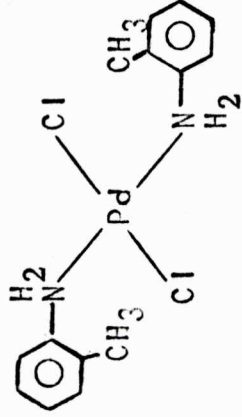
The $\text{trans-Pd}(\text{an})_2\text{Cl}_2$ was synthesized as previously reported (5). The remaining compounds were synthesized following a procedure developed by V. Wright (11). The syntheses of these compounds were performed several times in our laboratories and the products analyzed. Typically, the metal analysis agreed within $\pm 0.3\%$ of the theoretical (see Table II).

The general procedure followed in producing these palladium compounds is as follows (7):

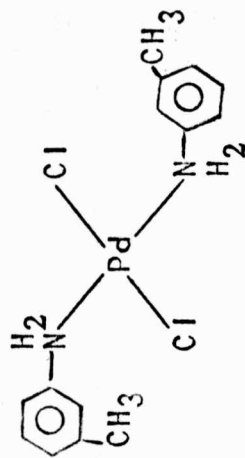
Six molar hydrochloric acid is added to palladium chloride and then slowly heated to dissolve the palladium chloride to form a solution of tetrachloropalladic acid, H_2PdCl_4 . An excess of the ligand, at least a four to one molar ratio of the ligand to the H_2PdCl_4 , is added to the cooled H_2PdCl_4 solution. At this point the reaction can follow one of two routes. One, a yellow or pale yellow-green solid of the $\text{trans-Pd}(\text{ligand})_2\text{Cl}_2$ would form immediately, or, secondly, a colorless to pale yellow green solution

TABLE I

STRUCTURE AND NOMENCLATURE OF SELECTED PALLADIUM COMPOUNDS

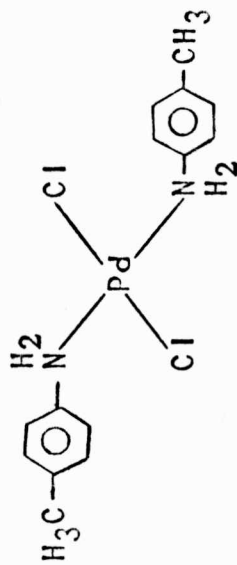
No.	Compound	Name
1.		trans-dichlorobis(aniline)palladium(II)
2.		trans-dichlorobis(o-toluidine)palladium(II)

3.



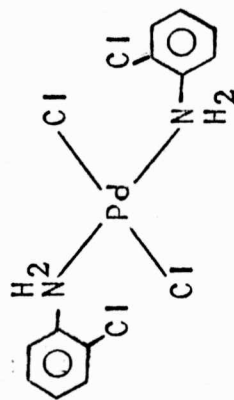
trans-dichlorobis(m-toluidine)palladium(II)

4.



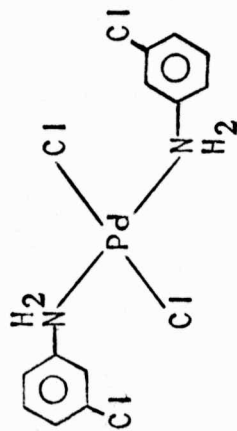
trans-dichlorobis(p-toluidine)palladium(II)

5.



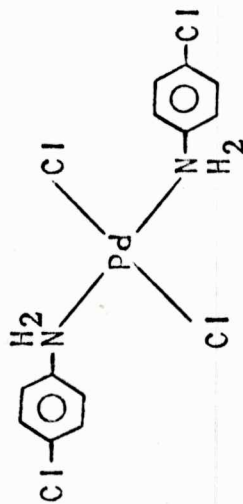
trans-dichlorobis(o-chloroaniline)palladium(II)

6.



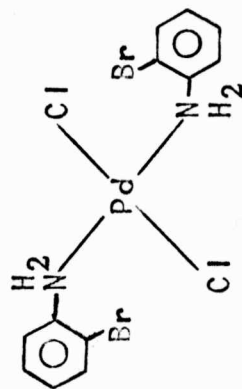
trans-dichlorobis(m-chloroaniline)palladium(II)

7.



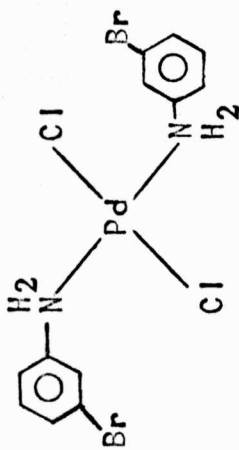
trans-dichlorobis(p-chloroaniline)palladium(II)

8.



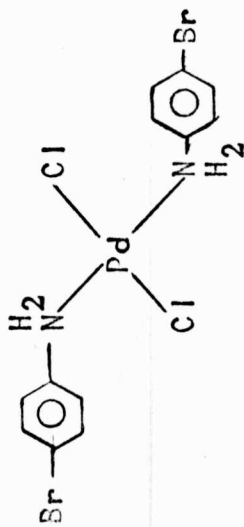
trans-dichlorobis(o-bromoaniline)palladium(II)

9.



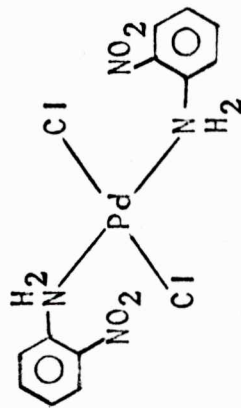
trans-dichlorobis(m-bromoaniline)palladium(II)

10.



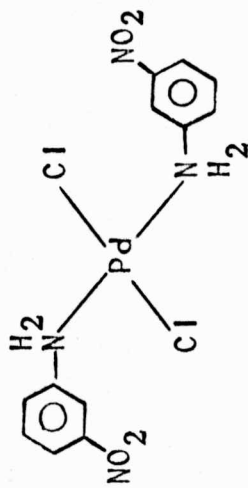
trans-dichlorobis(p-bromoaniline)palladium(II)

11.



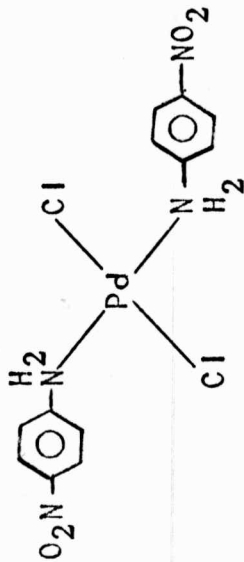
trans-dichlorobis(o-nitroaniline)palladium(II)

12.



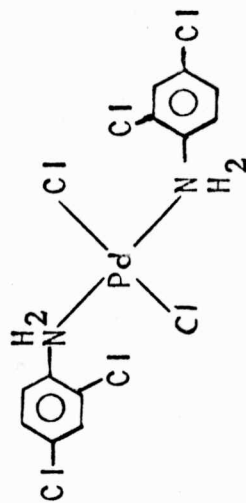
trans-dichlorobis(m-nitroaniline)palladium(II)

13.



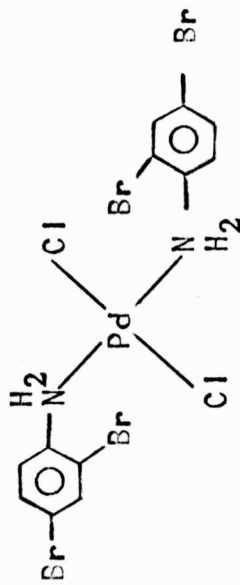
trans-dichlorobis(p-nitroaniline)palladium(II)

14.



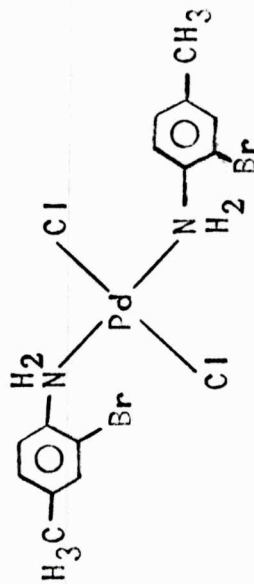
trans-dichlorobis(2,4-dichloroaniline)palladium(II)

15.



trans-dichlorobis(2,4-dibromoaniline)palladium(II)

16.



trans-dichlorobis(3-bromo-4-methyltoluene)amino)palladium(II)

TABLE II*

PER CENT PALLADIUM IN PALLADIUM COMPLEXES

No.	Compound	Theoretical		Experimental		Deviation %
		Pd %	Pd %	Pd %	Pd %	
1	trans-dichlorobis(aniline)palladium(II)	29.29	29.46 29.57	+0.17 +0.28		
2	trans-dichlorobis(o-toluidine)palladium(II)	27.81	28.04 27.77	+0.23 -0.04		
3	trans-dichlorobis(m-toluidine)palladium(II)	27.81	27.93 27.79	+0.12 -0.02		
4	trans-dichlorobis(p-toluidine)palladium(II)	27.81	27.85 27.80	+0.04 -0.01		
5	trans-dichlorobis(o-chloroaniline)palladium(II)	24.62	24.83 24.88	+0.21 +0.26		
6	trans-dichlorobis(m-chloroaniline)palladium(II)	24.62	24.70 24.52	+0.08 -0.10		
7	trans-dichlorobis(p-chloroaniline)palladium(II)	24.62	24.45 25.05	-0.17 +0.43		

*This data was compiled by V. Wright (11). The analysis was accomplished by ignition of the palladium complexes. Data was not available for trans-dichlorobis(2,4-dichloroaniline)palladium(II).

TABLE II (continued)

No.	Compound	Theoretical Pd %	Experimental Pd %	Deviation %
8	trans-dichlorobis(o-bromoaniline)palladium(II)	20.41	21.00 21.00	+0.59 +0.59
9	trans-dichlorobis(m-bromoaniline)palladium(II)	20.41	20.46 20.84	+0.05 +0.43
10	trans-dichlorobis(p-bromoaniline)palladium(II)	20.41	20.41 20.44	0.00 0.03
11	trans-dichlorobis(o-nitroaniline)palladium(II)	23.47	23.61 23.72	+0.14 +0.25
12	trans-dichlorobis(m-nitroaniline)palladium(II)	23.47	23.52 23.74	+0.05 +0.27
13	trans-dichlorobis(p-nitroaniline)palladium(II)	23.47	23.75 23.86	+0.28 +0.39
14	trans-dichlorobis(2,4-dichloroaniline)palladium(II)**			
15	trans-dichlorobis(2,4-dibromoaniline)palladium(II)	15.67	15.80 15.86	+0.13 +0.19
16	trans-dichlorobis(3-bromo-4-aminotoluene)palladium(II)	19.37	19.73 19.79	+0.36 +0.42

**This data was compiled by V. Wright. Data was not available for trans-dichlorobis(2,4-dichloroaniline)palladium(II). E

containing the soluble complex salt $\text{Pd}(\text{ligand})_4^{++} + 2 \text{Cl}^-$ can form. If the reaction follows the second path, enough 6M hydrochloric acid is added slowly to make the solution slightly acidic. The $\text{trans-Pd}(\text{ligand})_2\text{Cl}_2$ solid generally precipitated; however, in a few cases it was necessary to quench the reaction with water to precipitate the solid $\text{Pd}(\text{ligand})_2\text{Cl}_2$. The general procedure is outlined in Figure 1.

Synthesis of Trans-dichlorobis(aniline)palladium(II)

A volume of 35 ml. of 6M HCl was added to 1.2206 grams (6.8842×10^{-3} mole) PdCl_2 and then heated on a hot plate. The PdCl_2 dissolved in the HCl producing a solution of H_2PdCl_4 , which was dark red-brown in color. Then 23.0 ml. (2.5230×10^{-1} mole) of freshly distilled aniline was slowly added, while stirring, to the H_2PdCl_4 solution. A very bright yellow precipitate of $\text{trans-Pd}(\text{an})_2\text{Cl}_2$ formed. The precipitate was filtered with a fritted glass crucible and washed successively with 5 ml. each of water, absolute ethyl alcohol, and acetone. It was then air-dried for about five minutes and stored in a desiccator.

The remaining fifteen palladium compounds were synthesized in an analogous manner. The precipitate of each of the palladium compounds was separated, washed, dried, and stored as described above for the $\text{trans-dichlorobis}(\text{aniline})\text{palladium(II)}$ precipitate. The amounts of PdCl_2 , HCl, and ligand used in synthesizing each palladium compound is listed in Table III. The calculations used to determine the appropriate amounts of PdCl_2 and ligand are shown below using PdCl_2 and aniline as an example.

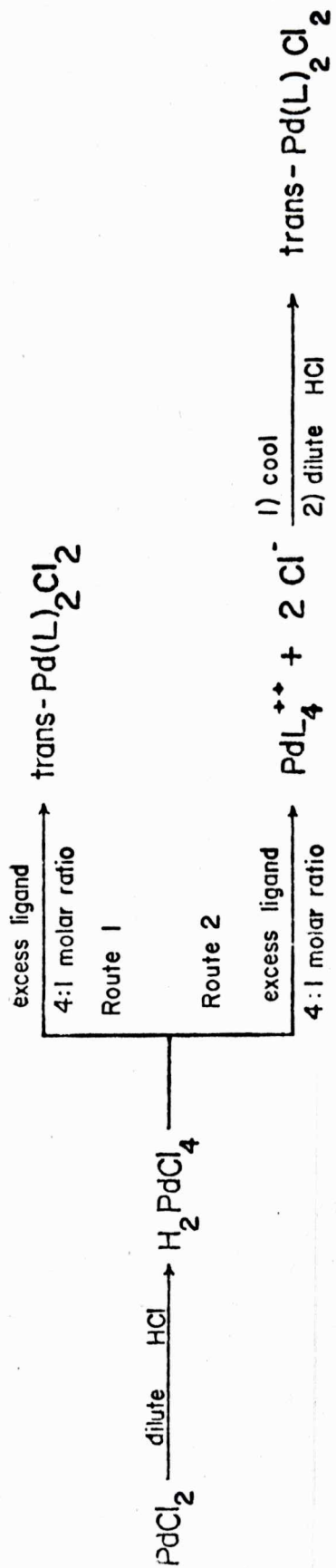


FIGURE 1

General Synthesis Of Palladium Complexes

The following calculations are shown as an example of the calculations used in synthesizing the palladium complexes. The calculations given for this example are those required to produce 2.0000 grams of $\text{Pd}(\text{an})_2\text{Cl}_2$.

molecular weight PdCl_2	177.31 g
molecular weight $\text{C}_6\text{H}_5\text{NH}_2$ (an)	93.129 g
molecular weight $\text{Pd}(\text{an})_2\text{Cl}_2$	363.568 g

$$2.0000 \text{ grams } \text{Pd}(\text{an})_2\text{Cl}_2 \times \frac{1 \text{ mole } \text{Pd}(\text{an})_2\text{Cl}_2}{363.568 \text{ grams } \text{Pd}(\text{an})_2\text{Cl}_2} =$$

$$5.5010 \times 10^{-3} \text{ mole } \text{Pd}(\text{an})_2\text{Cl}_2$$

To produce 5.5010×10^{-3} mole $\text{Pd}(\text{an})_2\text{Cl}_2$, 5.5010×10^{-3} mole PdCl_2 is needed.

$$5.5010 \times 10^{-3} \text{ mole } \text{PdCl}_2 \times \frac{177.31 \text{ grams } \text{PdCl}_2}{\text{mole } \text{PdCl}_2} = 9.7538 \times 10^{-1} \text{ gram } \text{PdCl}_2$$

For a 4 to 1 molar ratio of aniline to H_2PdCl_4 (made by dissolving the PdCl_2 in 6M HCl), 2.2004×10^{-2} mole of aniline is needed.

$$2.2004 \times 10^{-2} \text{ mole (an)} \times \frac{93.129 \text{ grams (an)}}{\text{mole (an)}} = 2.0492 \text{ grams (an)}$$

TABLE III

AMOUNTS OF PdCl₂, HCl, AND LIGANDS USED IN SYNTHESIS
OF THE PALLADIUM COMPLEXES

No.	Name of Compound	Mole of PdCl ₂	6M HCl (ml)	Mole of Ligand
1	trans-dichlorobis(aniline)palladium(II)	6.8842×10^{-3}	35	2.5230×10^{-1}
2	trans-dichlorobis(o-toluidine)palladium(II)	1.5959×10^{-3}	4	9.3216×10^{-2}
3	trans-dichlorobis(m-toluidine)palladium(II)	1.6011×10^{-3}	4	4.6608×10^{-2}
4	trans-dichlorobis(p-toluidine)palladium(II)	1.6344×10^{-3}	4	2.3803×10^{-2}
5	trans-dichlorobis(o-chloroaniline)palladium(II)	1.4483×10^{-3}	4	3.8091×10^{-2}
6	trans-dichlorobis(m-chloroaniline)palladium(II)	1.4652×10^{-3}	4	3.8091×10^{-2}
7	trans-dichlorobis(p-chloroaniline)palladium(II)	1.4455×10^{-3}	4	3.7923×10^{-2}
8	trans-dichlorobis(o-bromoaniline)palladium(II)	0.9550×10^{-3}	4	4.7770×10^{-3}
9	trans-dichlorobis(m-bromoaniline)palladium(II)	0.7095×10^{-3}	4	1.8361×10^{-2}

TABLE III (continued)

No.	Name of Compound	Mole of PdCl ₂	6M HCl (ml)	Mole of Ligand
10	trans-dichlorobis(p-bromoaniline)palladium(II)	1.1280 x 10 ⁻³	4	1.4521 x 10 ⁻²
11	trans-dichlorobis(o-nitroaniline)palladium(II)	1.4088 x 10 ⁻³	4	1.4594 x 10 ⁻²
12	trans-dichlorobis(m-nitroaniline)palladium(II)	1.4241 x 10 ⁻³	4	1.4525 x 10 ⁻²
13	trans-dichlorobis(p-nitroaniline)palladium(II)	1.4314 x 10 ⁻³	4	1.4207 x 10 ⁻²
14	trans-dichlorobis(2,4-dichloroaniline)palladium(II)	1.0293 x 10 ⁻³	4	1.2343 x 10 ⁻²
15	trans-dichlorobis(2,4-dibromoaniline)palladium(II)	0.9165 x 10 ⁻³	4	3.6843 x 10 ⁻³
16	trans-dichlorobis(3-bromo-4-aminotoluene)palladium(II)*			

*trans-dichlorobis(3-bromo-4-aminotoluene)palladium(II) was obtained from V. Wright. (11)

CHAPTER III
PREPARATION AND POLAROGRAPHIC ANALYSIS OF THE
TRANS-DICHLOROBIS(SUBSTITUTED ANILINE)PALLADIUM SOLUTIONS

Instrumentation and Procedure

All polarograms were obtained using a Heath Polarography Module, Model EUW-401. The polarographic cell used in this work was fitted with a three electrode system. The polarograms were recorded on a Beckman Electroscan 30. Some typical polarograms of the electrolysis palladium complex solutions have been given in the Appendix (see Figures 2-9). Also, one polarogram which exhibited an erratic drop-rate similar to that described by Willis (10) has been shown (see Figure 10). Since it has been found that the temperature coefficient of the diffusion current in dimethylformamide is rather large (3), a temperature control was critical. Polarograms of each of the solutions were run at $25 \pm 0.2^\circ$. This was accomplished by circulating water from a constant-temperature water bath through a copper coil for fifteen minutes before the polarogram was run. The copper coil was fitted in a beaker of water which surrounded the polarographic cell. The electrolysis solutions were deaerated by bubbling tank nitrogen through them for approximately fifteen minutes.

Materials

The electrolysis palladium complex solutions were made $10^{-3}M$; N,N-Dimethylformamide was used as the solvent. The dimethylformamide, reagent grade, was obtained from the Fisher Scientific Company. Anhydrous

potassium perchlorate was found to be quite soluble in dimethylformamide at 25°. It was used at 10^{-1} M concentration, as the non-complexing, supporting electrolyte for each of the electrolysis solutions.

The solutions were prepared by dissolving the appropriate amounts of each palladium complex and potassium perchlorate in dimethylformamide and adding enough dimethylformamide to give a final volume of 50.0 ml. These amounts are listed in Table IV. Triton 100-X was used as a maximum suppressor.

The polarograms were run at a current setting of 1.0 μ a. A scan from + 0.25 to - 0.35 volt was made for each polarographic reduction. The half-wave potentials ($E_{1/2}$) and the number of electrons (n) involved in the reduction step were determined by plots of E versus $\log \frac{i}{i_d - i}$ (4). The values of $E_{1/2}$ and n obtained by these plots are expressed relative to the saturated calomel electrode and are listed in Table V.

Results and Discussion

Shortly after the discovery of the reducibility or oxidizability of certain organic compounds at a dropping mercury electrode, a search began for relations between the polarographic behavior of organic substances and their structure. Shikata and Tachi (6) made the first attempt to describe the effects of substituents on half-wave potentials in the reduction of organic compounds. They proposed the "electronegativity rule", which states that the more electronegative the substituent, the more positive the half-wave potential. Electronegativity was described in terms of the effect on the dissociation of benzoic acid when substituents were introduced into the para position.

TABLE IV
 AMOUNTS OF PALLADIUM COMPLEX AND POTASSIUM PERCHLORATE USED IN
 PREPARATION OF SOLUTIONS FOR POLAROGRAPHIC STUDY

No.	Name of Compound	Amount of Pd Compound for 10^{-3} M (in g)	Amount of KClO ₄ for 10^{-1} M (in g)
1	trans-dichlorobis(aniline)palladium(II)	0.0182	0.6928
2	trans-dichlorobis(o-toluidine)palladium(II)	0.0196	0.6928
3	trans-dichlorobis(m-toluidine)palladium(II)	0.0196	0.6928
4	trans-dichlorobis(p-toluidine)palladium(II)	0.0196	0.6928
5	trans-dichlorobis(o-chloroaniline)palladium(II)	0.0216	0.6928
6	trans-dichlorobis(m-chloroaniline)palladium(II)	0.0216	0.6928
7	trans-dichlorobis(p-chloroaniline)palladium(II)	0.0216	0.6928
8	trans-dichlorobis(c-bromoaniline)palladium(II)	0.0261	0.6928
9	trans-dichlorobis(m-bromoaniline)palladium(II)	0.0261	0.6928

TABLE IV (continued)

No.	Name of Compound	Amount of Pd Compound for 10^{-3} M (in g)	Amount of $KClO_4$ for 10^{-1} M (in g)
10	trans-dichlorobis(p-bromoaniline)palladium(II)	0.0261	0.6928
11	trans-dichlorobis(o-nitroaniline)palladium(II)	0.0227	0.6928
12	trans-dichlorobis(m-nitroaniline)palladium(II)	0.0227	0.6928
13	trans-dichlorobis(p-nitroaniline)palladium(II)	0.0227	0.6928
14	trans-dichlorobis(2,4-dichloroaniline)palladium(II)	0.0251	0.6928
15	trans-dichlorobis(2,4-dibromoaniline)palladium(II)	0.0340	0.6928
16	trans-dichlorobis(3-bromo-4-aminotoluene)palladium(II)	0.0275	0.6928

TABLE V
 HALF-WAVE POTENTIALS OF THE PALLADIUM COMPLEXES
 IN N,N-DIMETHYLFORMAMIDE*

No.	$10^{-3}\text{M Pd(L)}_2\text{Cl}_2$ and 10^{-4}M KClO_4 Solution in DMF	$E_{1/2}$ at $1.0 \mu\text{a}$	No. of Electrons (n)
1	trans-dichlorobis(aniline)palladium(II)	-0.12	1.00
2	trans-dichlorobis(o-toluidine)palladium(II)	-0.16	0.79
3	trans-dichlorobis(m-toluidine)palladium(II)	-0.14	1.25
4	trans-dichlorobis(p-toluidine)palladium(II)	-0.13	1.36
5	trans-dichlorobis(o-chloroaniline)palladium(II)	-0.10	1.01
6	trans-dichlorobis(m-chloroaniline)palladium(II)	-0.11	1.00
7	trans-dichlorobis(p-chloroaniline)palladium(II)	-0.11	1.15
8	trans-dichlorobis(o-bromoaniline)palladium(II)	-0.13	1.27

*Solutions of the palladium complexes were made 10^{-3}M and the supporting electrolyte KClO_4 10^{-4}M . The solvent was DMF.

TABLE V (continued)

No.	$10^{-3}\text{M Pd(L)}_2\text{Cl}_2$ and 10^{-1}M KClO_4 Solution in DMF	$E_{1/2}$ at $1.0 \mu\text{a}$	No. of Electrons (n)
9	trans-dichlorobis(m-bromoaniline)palladium(II)	-0.14	0.98
10	trans-dichlorobis(p-bromoaniline)palladium(II)	-0.12	1.25
11	trans-dichlorobis(c-nitroaniline)palladium(II)	-0.16	0.98
12	trans-dichlorobis(m-nitroaniline)palladium(II)	-0.15	0.75
13	trans-dichlorobis(p-nitroaniline)palladium(II)	-0.15	0.74
14	trans-dichlorobis(2,4-dichloroaniline)palladium(II)	-0.15	1.09
15	trans-dichlorobis(2,4-dibromoaniline)palladium(II)	-0.14	0.87
16	trans-dichlorobis(3-bromo-4-aminotoluene)palladium(II)	-0.16	0.78

Efforts were later made to explain the changes in the polarographic waves in terms of concepts developed to describe the different types of electron displacement occurring in organic molecules under the influence of substituents. Inductive (I_S) and inductomeric (I_D) effects express the displacement of electrons in one direction in the molecule. Substituents or external electric fields (resulting from the presence of another molecule) cause such effects. Mesomeric (M) and electromeric (E) effects have also been considered for systems involving $\pi - \pi$ or $\pi - p$ conjugation. These effects, mesomeric and electromeric, express the effect of a shift of an electron pair under the influence of a substituent or of an external field. Inductive and inductomeric effects are expressed simply as inductive effects (I) and mesomeric and electromeric effects as tautomeric effects (T).

Hydrogen is used to express the relative effect of a substituent (13). If the substituent is electrophilic, i.e., more electronegative than the hydrogen atom, the effect is taken as negative (-I, -T). However, if the group is nucleophilic, i.e., less electronegative than the hydrogen atom, and repels electrons, the resulting effect is taken as positive (+I, +T). The effects of some common substituents are summarized in Table VI.

The following two rules have been recognized for reduction processes for which the potential is determined by a nucleophilic process (12):

1. Groups with -I and -T effects shift the half-wave potentials toward more positive values. Groups with +I and +T effects shift the half-wave potentials toward more negative values.

2. In the absence of other effects, the reduction of benzene derivatives with a reducible group in the side chain and a -T substituent in the ortho or para position occurs at more positive potentials than that of the meta isomer. On the other hand, in the presence of a +T group, the reduction of the meta derivatives takes place at a more positive potential than that of the ortho or para isomer.

Substituent effects on half-wave potentials can be treated in a way that has been used for the quantitative treatment of substituent effects in groups of compounds of the type X-Y-R, where the reactive group R undergoes electroreduction under specified reaction conditions. The compounds compared in a given reaction series differ only in the kind of the substituent X, which is not directly involved in the reaction.

In a properly chosen reaction series the mechanism of the electrode process is the same for all members of the series; also, the values of the transfer coefficient of various members of the reaction series vary only slightly. If properly chosen, this reaction series allows accurate comparison of half-wave potentials. All values intended for structural correlations must be obtained under identical experimental conditions with particular emphasis on identical supporting electrolytes (13).

The experimental conditions were kept constant throughout all of the polarographic reductions. The values of n , the number of electrons transferred in the reduction step, observed were obtained by plots of E versus $\log \frac{i}{i_d - i}$. The value of the number of electrons, n , was calculated to be in the range of 0.74 to 1.36 electrons. Despite the range

TABLE VI

EFFECTS OF SOME COMMON SUBSTITUENTS

NH ₂	-I	+T
CH ₃	+I	+T
Cl	-I	+T
Br	-I	+T
NO ₂	-I	-T

Source: P. Zuman, Substituent Effects In Organic Polarography (New York: Plenum Press, 1967), p. 3. (13)

TABLE VII

DISSOCIATION CONSTANTS OF SOME ORGANIC BASES
IN AQUEOUS SOLUTIONS

Amine	K _b
aniline	3.82 × 10 ⁻¹⁰
o-toluidine	2.47 × 10 ⁻¹⁰
m-toluidine	4.92 × 10 ⁻¹⁰
p-toluidine	1.18 × 10 ⁻⁹
o-chloroaniline	3.71 × 10 ⁻¹²
m-chloroaniline	2.88 × 10 ⁻¹¹
p-chloroaniline	8.45 × 10 ⁻¹¹
o-nitroaniline	6 × 10 ⁻⁴
m-nitroaniline	2.7 × 10 ⁻⁵

Source: R. C. Weast, S. M. Selby, C. D. Hodgman, eds., Handbook of Chemistry and Physics, 46th Edition (Cleveland, Ohio: The Chemical Rubber Co., 1965), p. D-77. (9)

of values for n , it was assumed, for initial comparisons, that the electrode process for the reduction step observed was the same in each of the palladium complexes.

Most substituent effects on half-wave potentials can be expressed by equation (i)

$$\Delta E_{1/2} = P + M + S \quad (i)$$

where P represents the shift in the half-wave potential due to the change in the polar activation energy increment, M is the shift in the half-wave potential resulting from the change in the mesomeric energy increment, and, S is the shift in the half-wave potential due to the change in the total steric energy increment.

For a group of substances in which both the steric and mesomeric effects are negligible or practically constant, the substituent effect can be assumed to be polar only. Compounds in which the reactive group and the substituent are separated by an aromatic ring must exclude ortho-substituted derivatives for steric effects to be negligible. Also, mesomeric interaction between the reactive group and the substituent which takes place via the aromatic ring have to be excluded. When these conditions are met the polar effect P can be expressed by the Hammett equation (ii)

$$P = \rho_R \sigma_X \quad (ii)$$

and equation (i) becomes

$$\Delta E_{1/2} = \rho_{\pi,R} \sigma_X \quad (iii)$$

In equation (iii) the term σ_X stands for the total polar substituent constant. This constant is independent of the type of reactive group R, of the reaction conditions, and of the reaction involved; but, it is dependent upon the position and kind of substituent.

The reaction constant $\rho_{\pi,R}$ depends on the kind of electroactive group R, on the temperature, and on the composition of the supporting electrolyte; but, it is independent of the kind and position of the substituents. In the reaction series studied, the electroactive group in every case was the NH_2 group. Therefore, the value of the reaction constant $\rho_{\pi,R}$ was taken to be constant throughout the series.

The value of the substituent constants (13) listed in Table VIII were used to make plots of $E_{1/2}$ versus σ_X . If there is a correlation between the shift of the half-wave potential ($\Delta E_{1/2}$) and the substituent constant (σ_X), a straight line should be obtained when the values of $E_{1/2}$ are plotted against the σ_X values. A straight line was obtained when a plot of $E_{1/2}$ versus σ_X values was made (see Figures 11 and 12 in the Appendix). The straight line was obtained by the Method of Least Squares and linear correlation coefficients were determined by use of the Product-Moment Formula (8). From the value of the linear correlation coefficient for the straight line plot of $E_{1/2}$ versus σ_p one could suggest that the plot might possibly be reliable. For the plot of $E_{1/2}$ versus σ_p to be more reliable, additional experimental $E_{1/2}$ values of the para substituted palladium compounds would be needed. From the value of the linear correlation coefficient for the plot of $E_{1/2}$ versus σ_m one would assume the straight line plot of $E_{1/2}$ versus σ_m to be more reliable.

TABLE VIII
SELECTED VALUES OF SUBSTITUENT CONSTANTS
THERMODYNAMIC VALUES ACCURATE WITHIN ± 0.02 σ UNITS

Group	σ_{m-X}	σ_{p-X}
CH ₃	-0.07	-0.17
Cl	+0.37	+0.23
Br	+0.39	+0.23
NO ₂	+0.71	+0.78

Source: P. Zuman, Substituent Effects In Organic Polarography
(New York: Plenum Press, 1967), pp. 46-48. (13)

According to the effects shown in Table VI, the ortho, meta, and para isomers of trans-dichlorobis(toluidine)palladium(II) solutions (compounds 2, 3, and 4) should shift the $E_{1/2}$ to more negative values than the $E_{1/2}$ value of trans-dichlorobis(aniline)palladium(II), compound 1. The experimental $E_{1/2}$ values of compounds 2, 3, and 4 were found to be more negative than the $E_{1/2}$ value of compound 1.

As stated previously, concerning Willis' work (10), the more basic the amine the more negative the value of $E_{1/2}$. From the K_b values of Table VII one would predict that the meta and para isomers of trans-dichlorobis(toluidine)palladium(II) solutions (compounds 3 and 4) should have more negative $E_{1/2}$ values than the $E_{1/2}$ value of compound 1. Using Table VII, an $E_{1/2}$ value more positive than the $E_{1/2}$ value of compound 1 would be predicted for compound 2, trans-dichlorobis(o-toluidine)palladium(II). However, the experimental $E_{1/2}$ value of compound 2 was more negative than the $E_{1/2}$ value of compound 1.

From the values of Table VI one would predict that the ortho, meta, and para isomers of trans-dichlorobis(nitroaniline)palladium(II) solutions (compounds 11, 12, and 13) should shift the $E_{1/2}$ to values more positive than the $E_{1/2}$ value of compound 1. The experimental $E_{1/2}$ values did not conform to the $E_{1/2}$ shift predicted from the values listed in Table VI because the experimental $E_{1/2}$ values of compounds 11, 12, and 13 were found to be more negative than the $E_{1/2}$ value of compound 1. However, the experimental $E_{1/2}$ values of compounds 11, 12, and 13 conformed to the shift in $E_{1/2}$ predicted by the use of Table VII.

The ortho, meta, and para isomers of trans-dichlorobis(chloroaniline) palladium(II) and trans-dichlorobis(bromoaniline)palladium(II) solutions (compounds 5, 6, 7, and 8, 9, 10 respectively) as shown by Table VI have a +I but a -T value. Therefore, it would be difficult to predict, by the use of Table VI, whether the values of $E_{1/2}$ of compounds 5, 6, 7, 8, 9, and 10 would be more positive or more negative than the $E_{1/2}$ values of compound 1. The experimental $E_{1/2}$ values of compounds 5, 6, and 7 conform to the $E_{1/2}$ shift one would predict by the use of K_D values from Table VII.

Conclusions

The problem has been approached with the assumption that the substituent effect is due to the polar effect only. A plot of $E_{1/2}$ versus σ_p gave a straight line, but the reliability of this plot is questionable. The plot of $E_{1/2}$ versus σ_m gave a straight line of much greater reliability. Therefore, a correlation between the $E_{1/2}$ shifts and the meta substituents might safely be assumed. It also has been found that the $E_{1/2}$ shifts of some of the palladium complexes conform to the shifts predicted by the use of Tables VI and VII.

From the range of values of the number of electrons, the electrode process could be more complex than was originally assumed. An area for future investigation could include a more detailed study of the reaction series in another organic solvent such as acetonitrile.

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APPENDIX

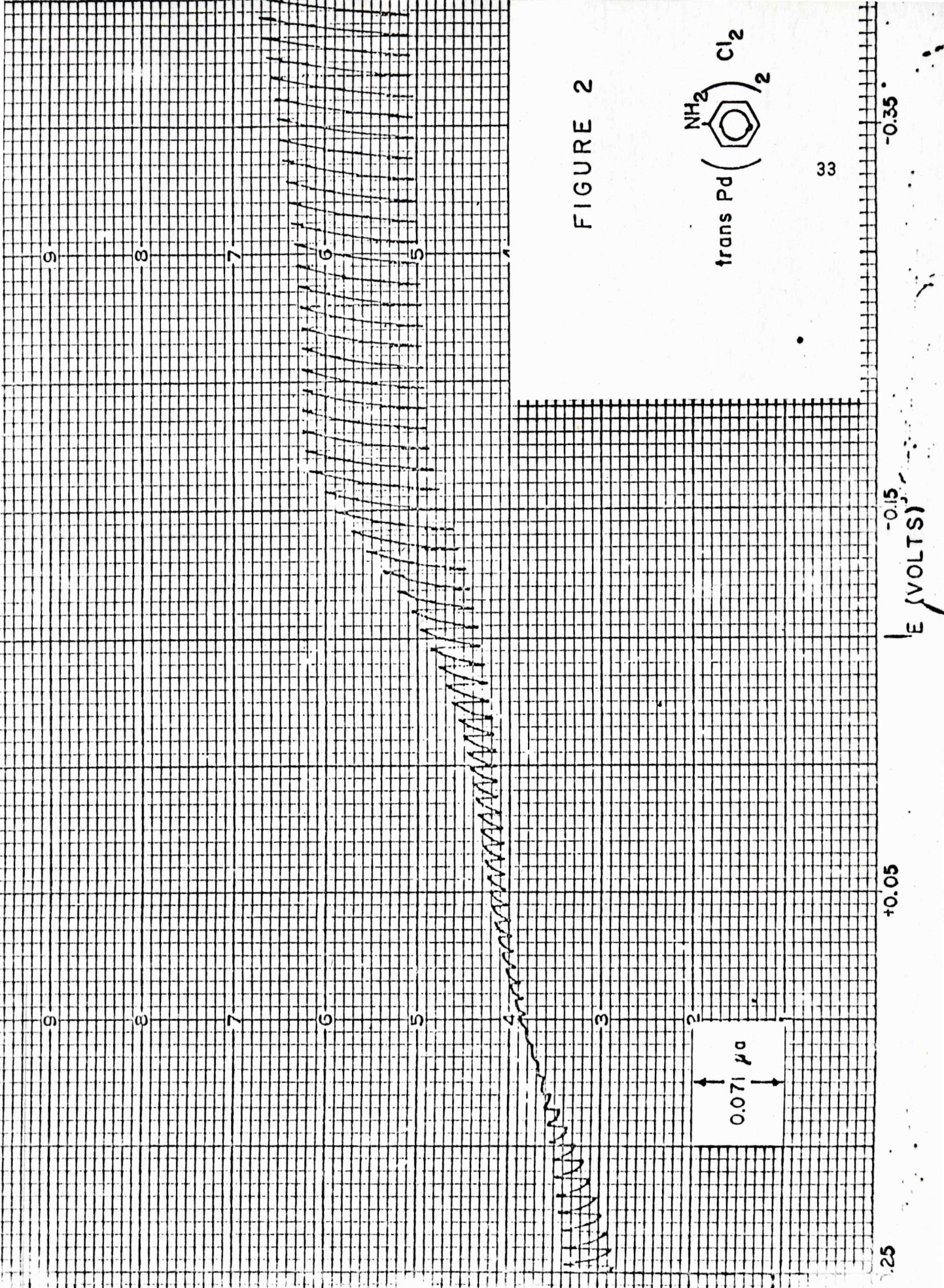
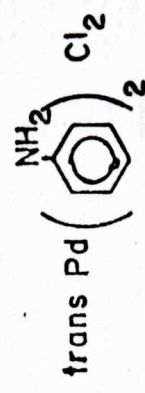


FIGURE 2



33

9

8

7

6

5

4

3

2

1

+0.25

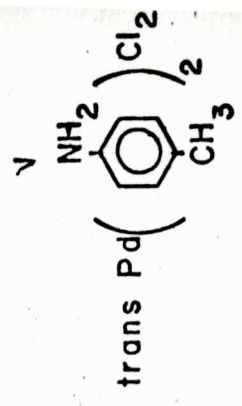
+0.05

-0.15

-0.35

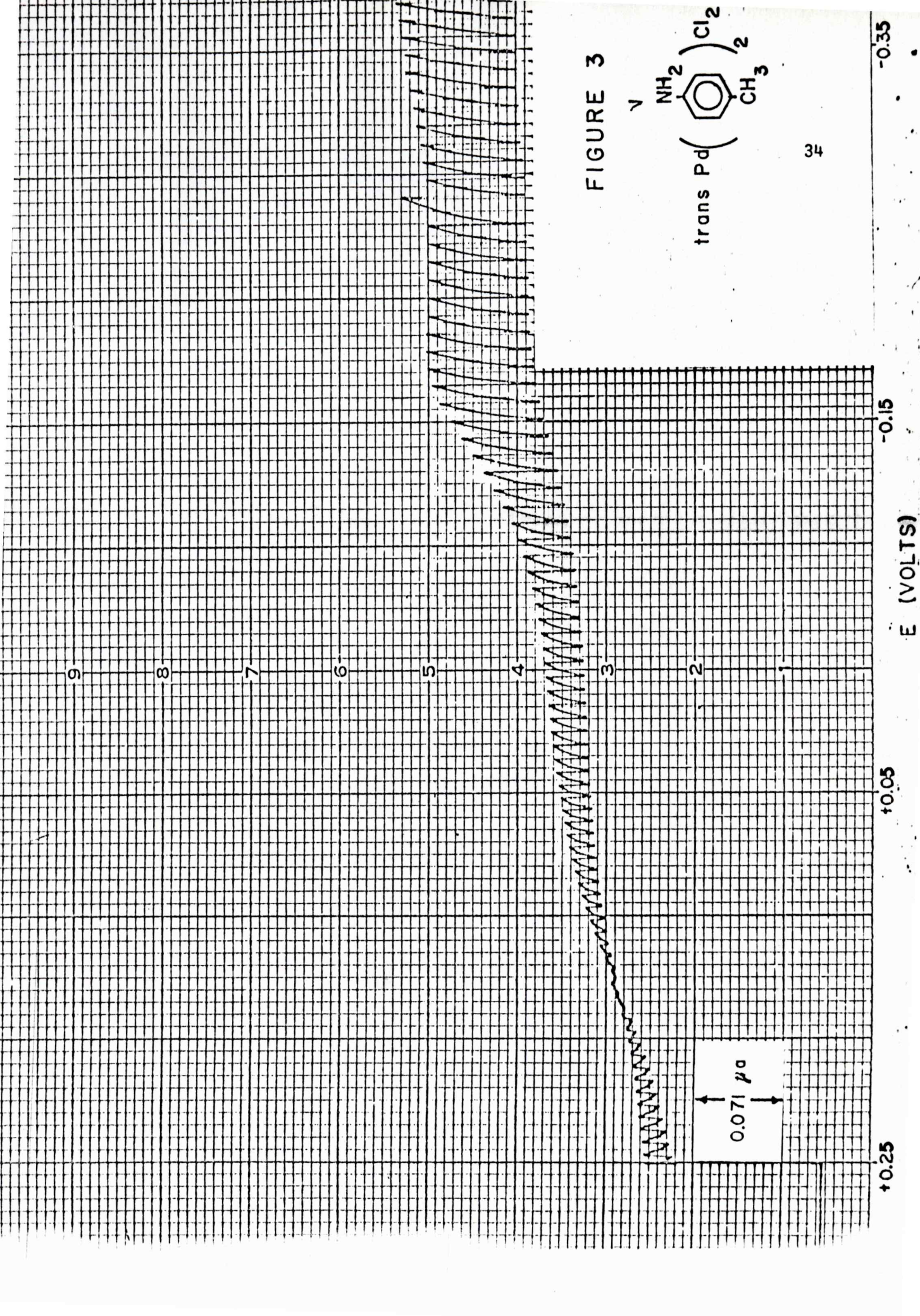
E (VOLTS)

FIGURE 3



34

0.071 μa



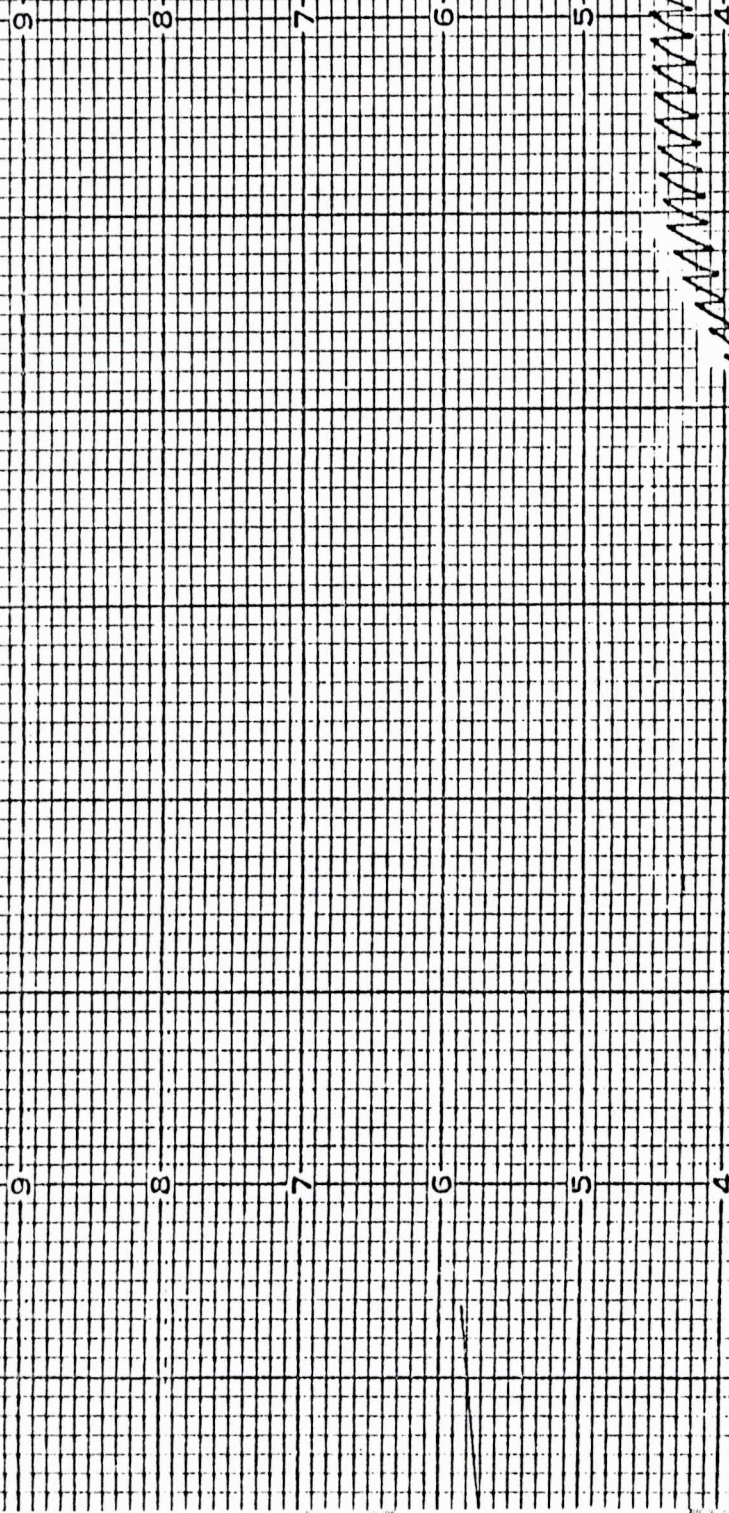
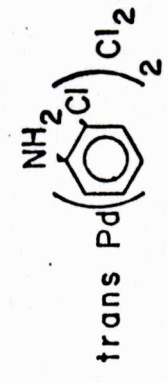


FIGURE 4



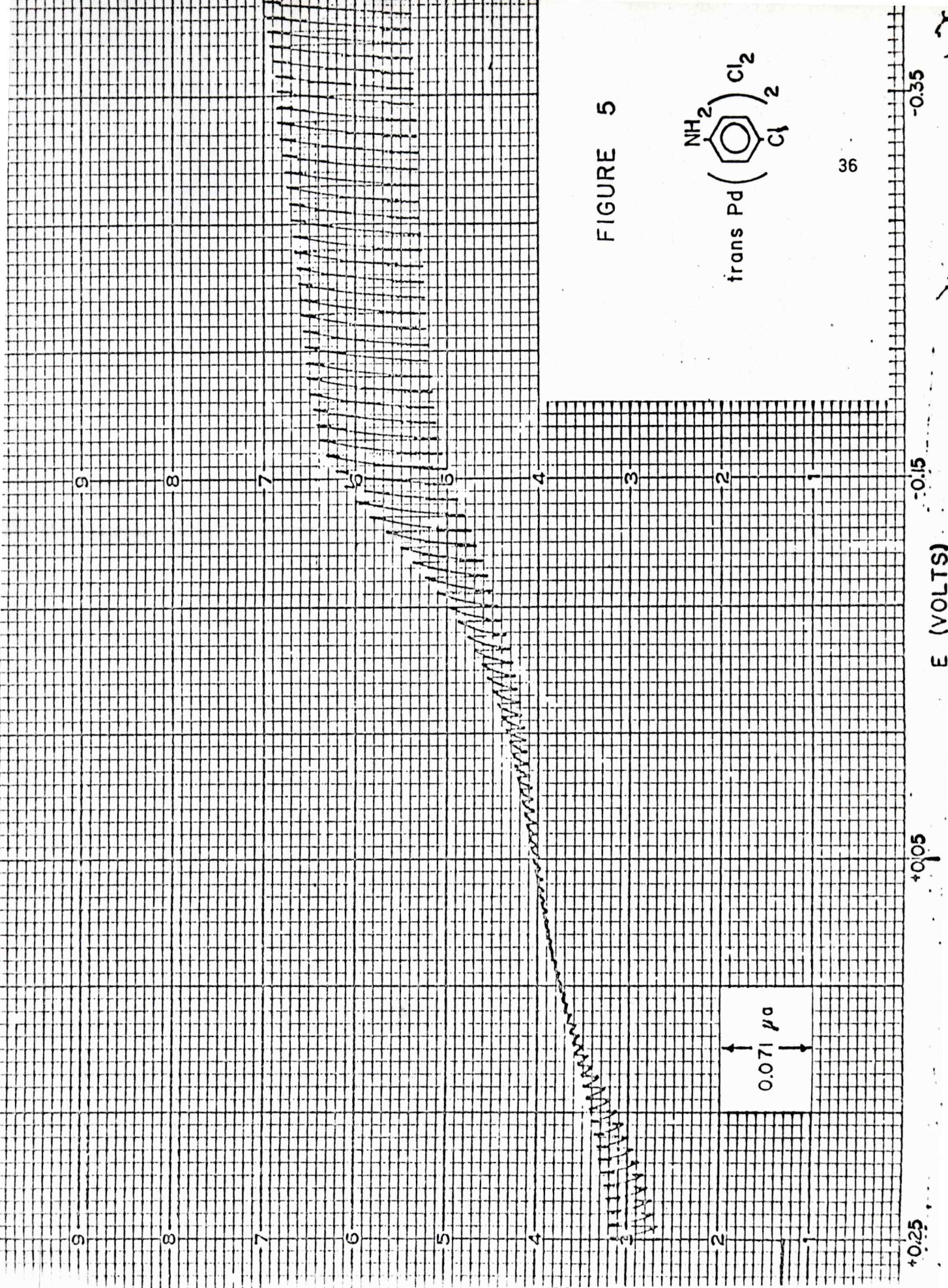
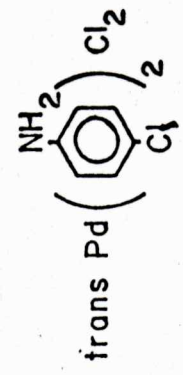


FIGURE 5



+0.25

+0.05

-0.15

-0.35

E (VOLTS)

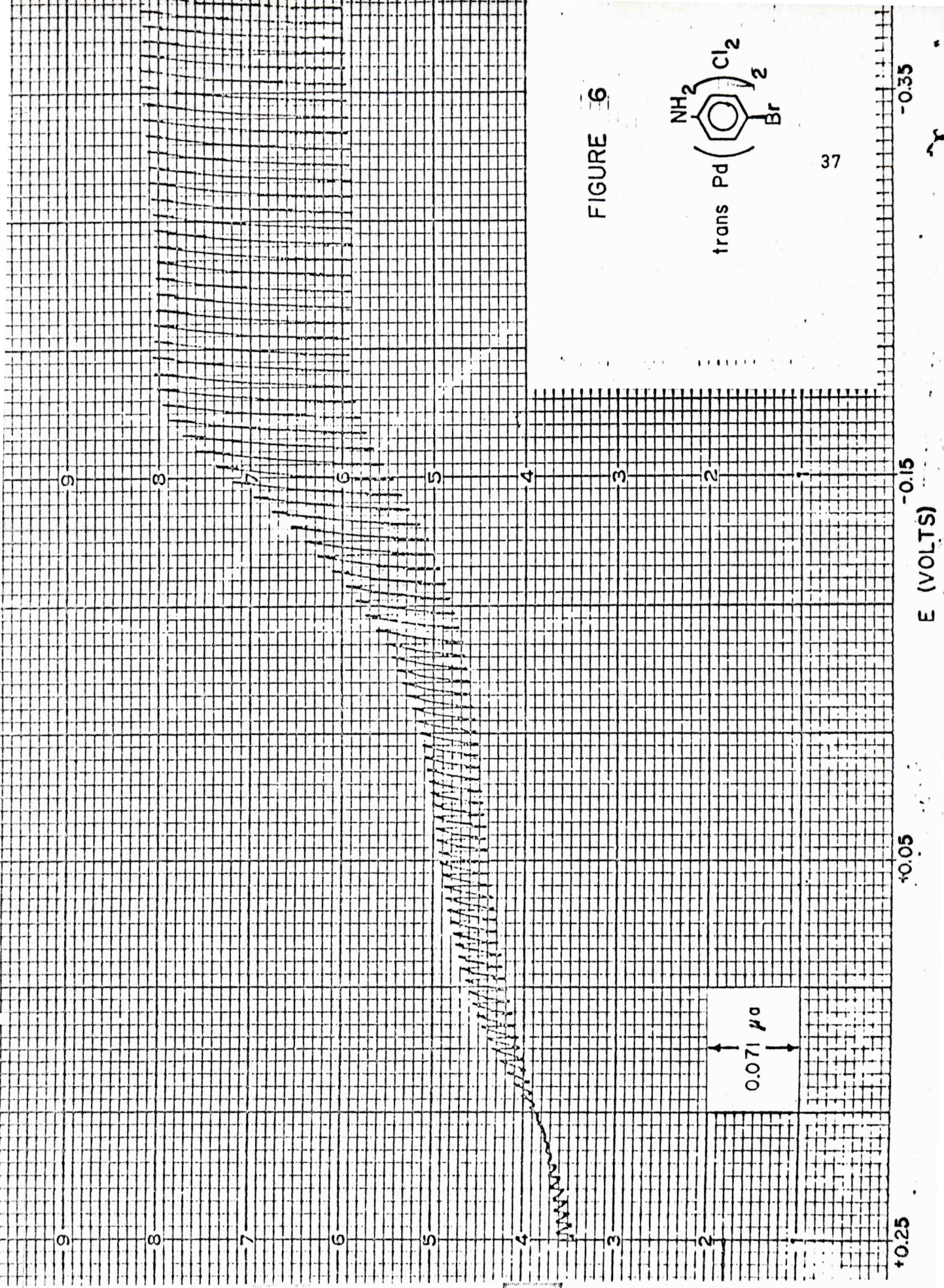
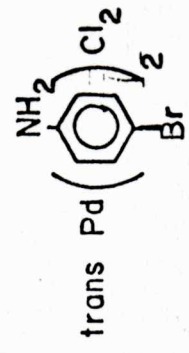


FIGURE 6



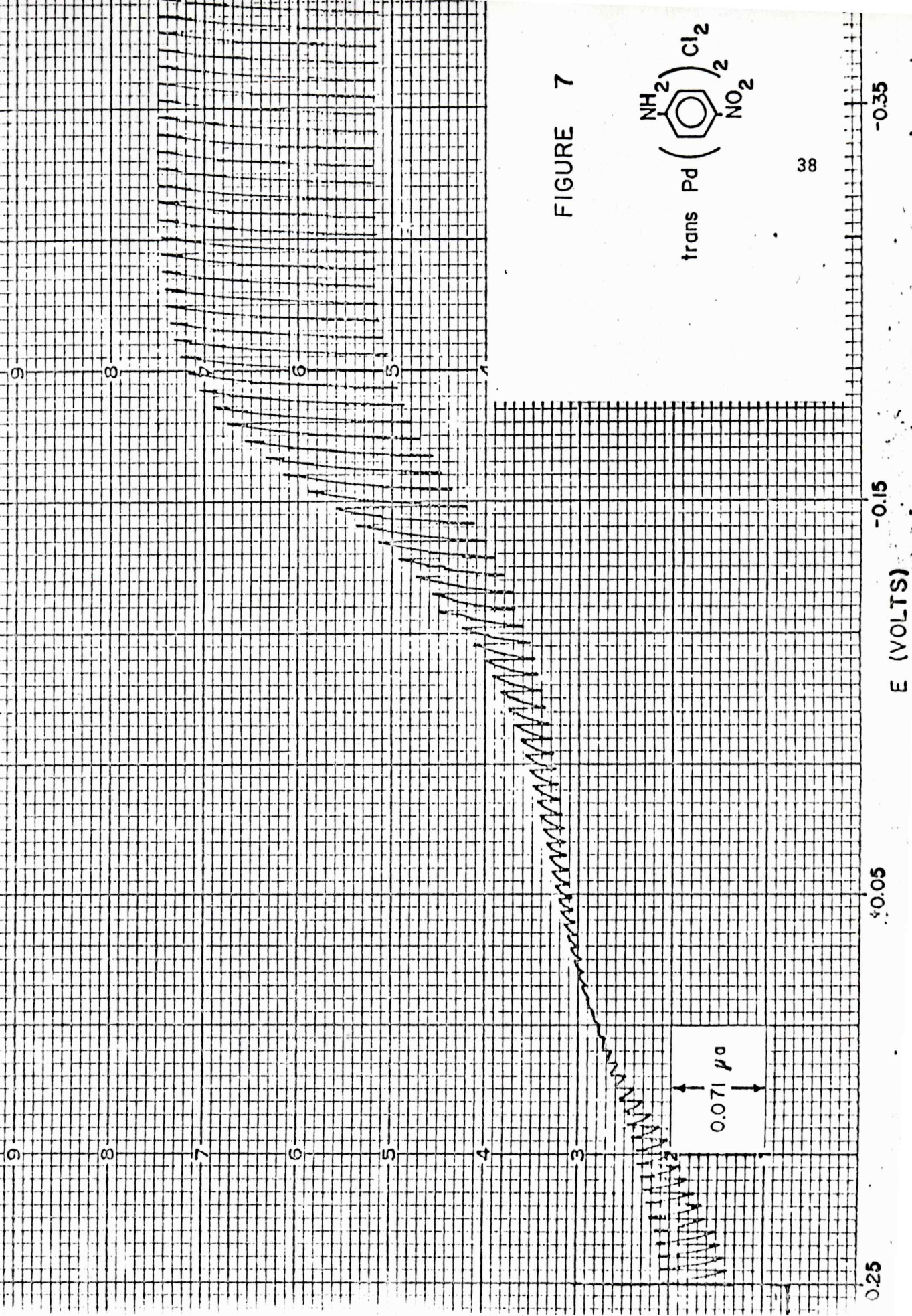
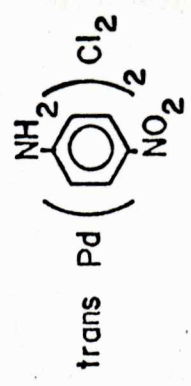


FIGURE 7



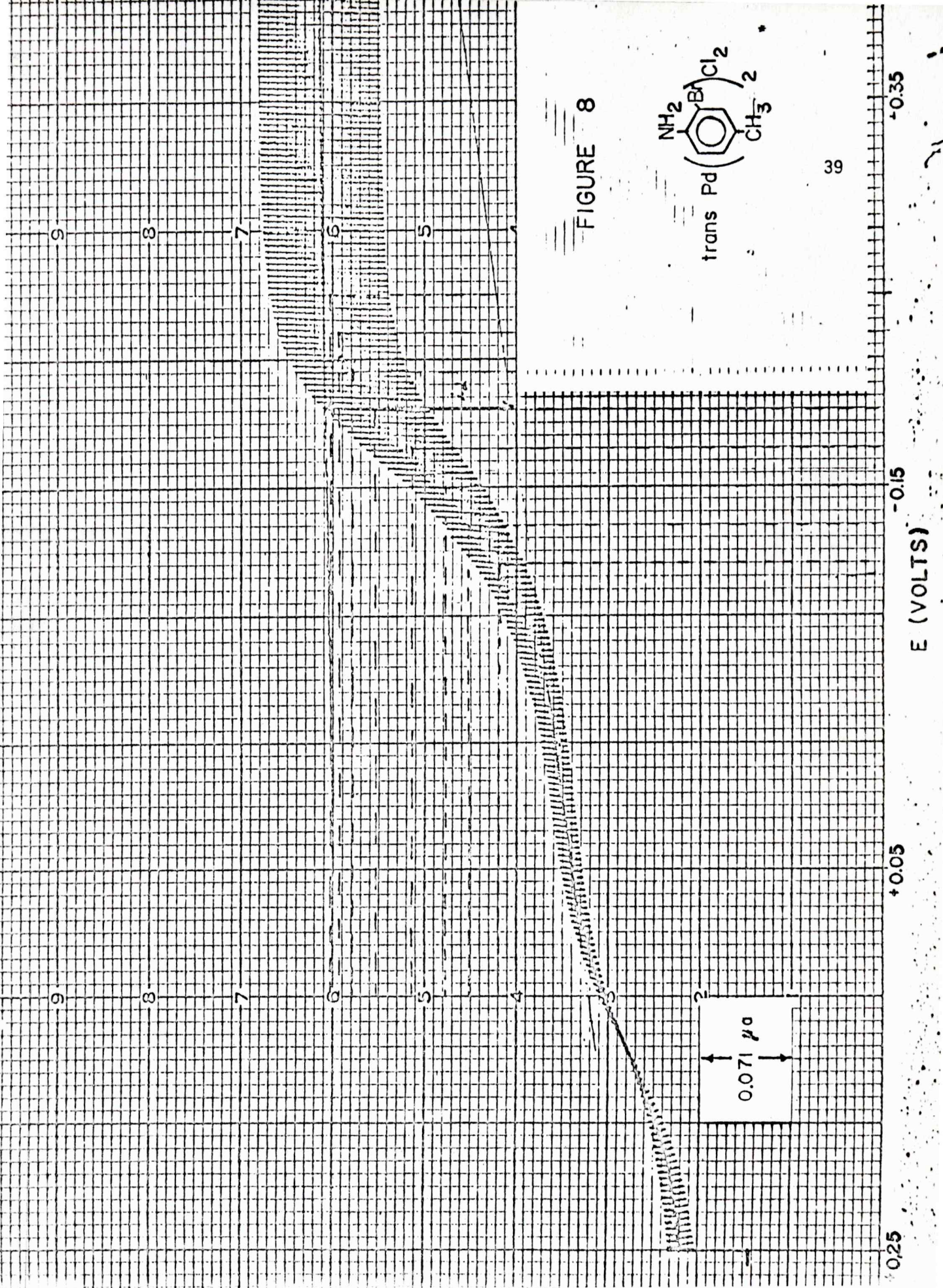
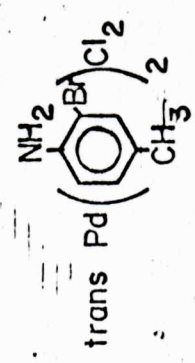


FIGURE 8



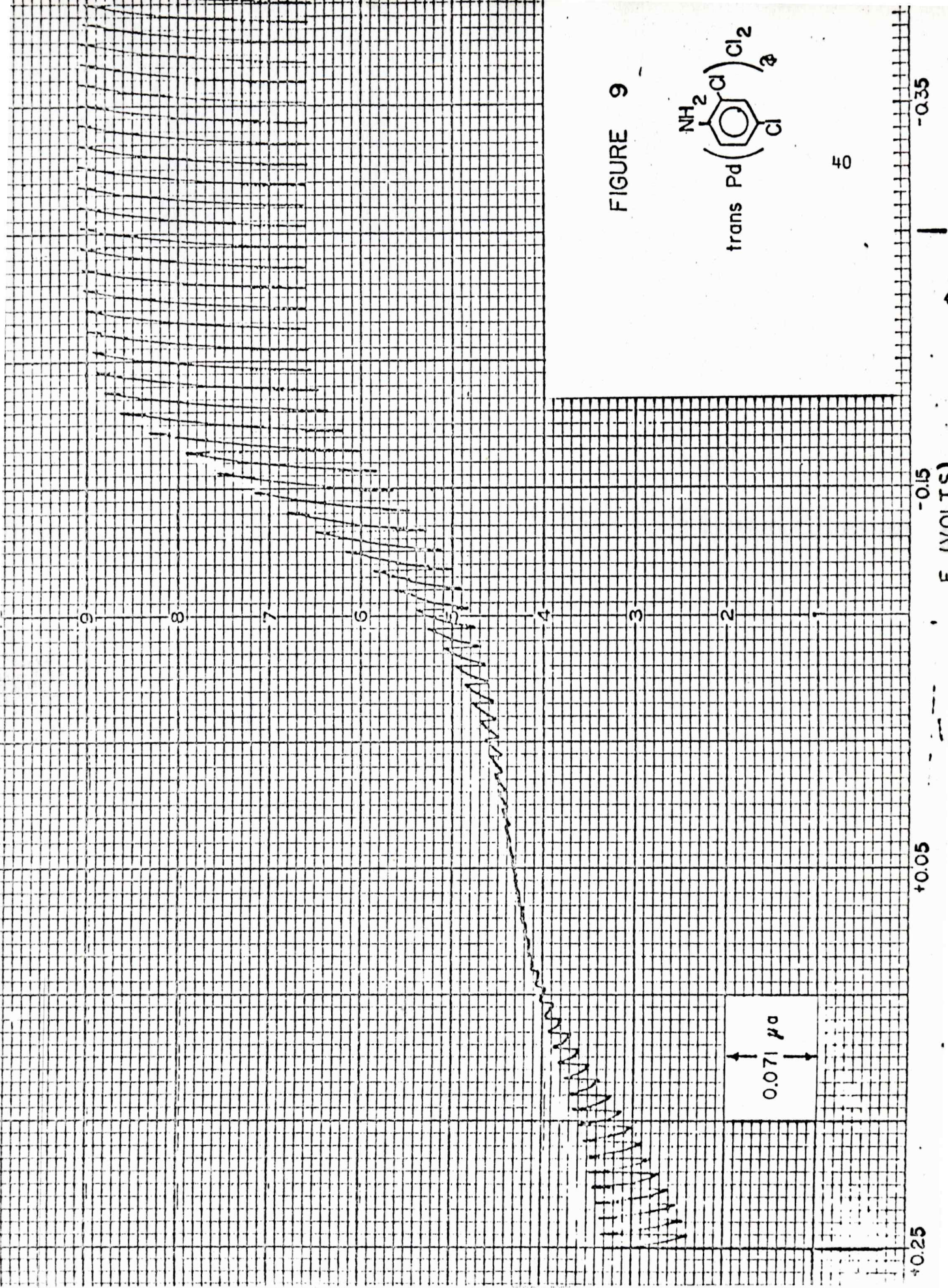
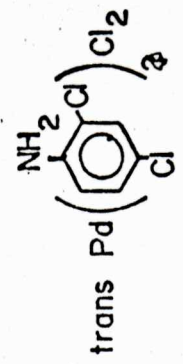


FIGURE 9



40

0.071 $\mu\sigma$

+0.25

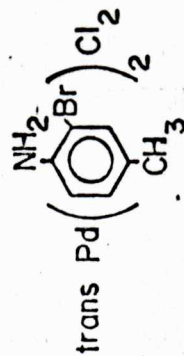
+0.05

-0.15

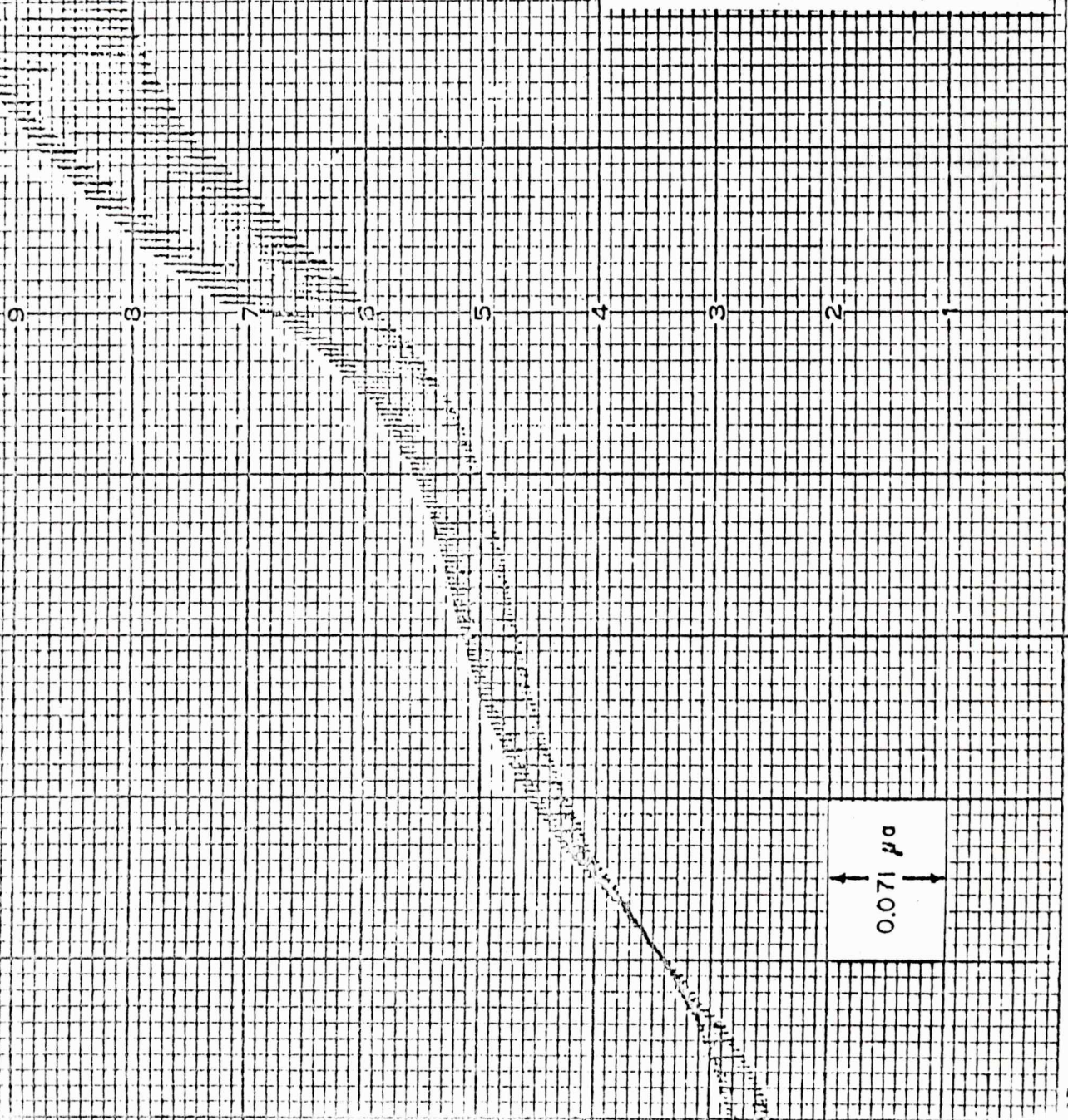
-0.35

5 (A.U.T.S)

FIGURE 10



F₁



+0.05 -0.15 -0.35

E (VOLTS)

5

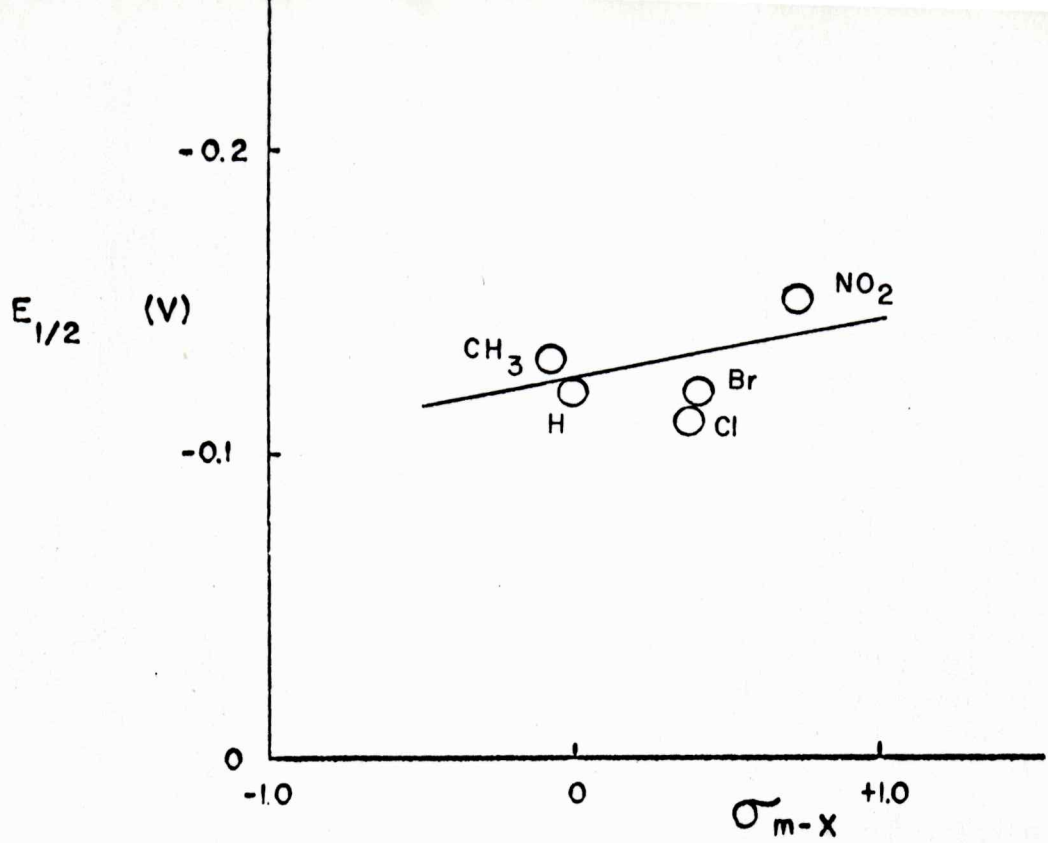


FIGURE 11

PLOT OF $E_{1/2}$ VS σ_{m-X}

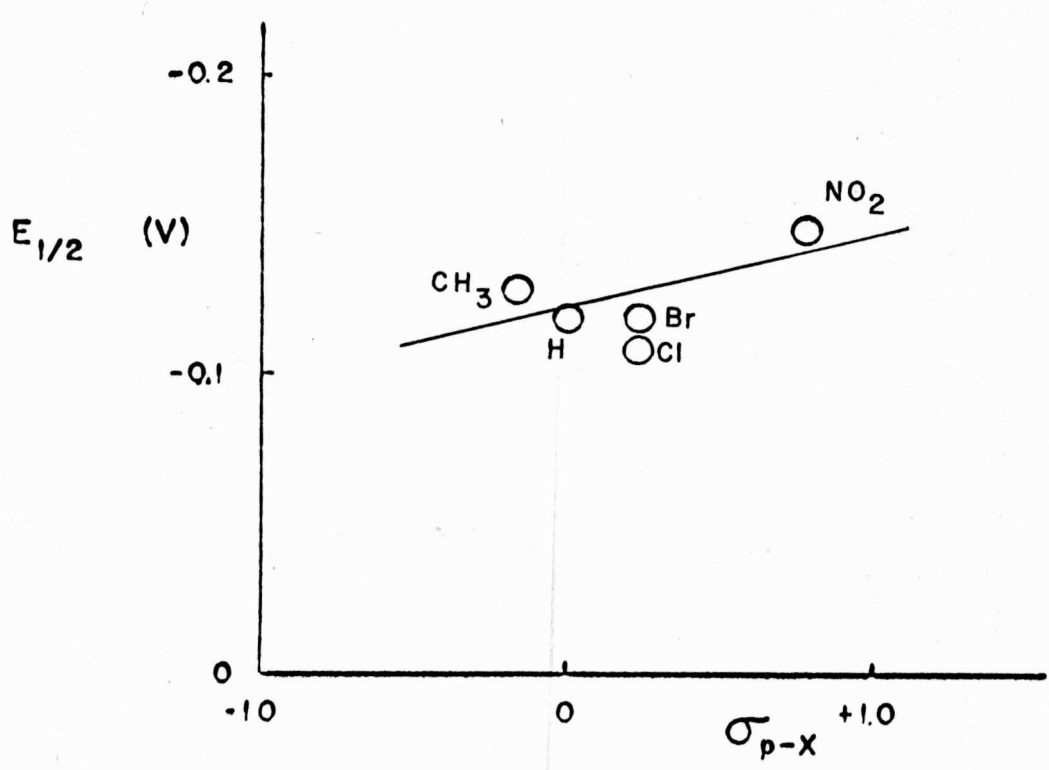


FIGURE 12

PLOT OF $E_{1/2}$ VS σ_{p-X}