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AD

Report Number 2

FUNDAMENTAL STUDIES IN ELECTROCHEMISTRY

Quarterly Progress Report  
15 March 1966 - 14 June 1966.

by

Bruce Campbell  
K. S. V. Santhanam  
Allen J. Bard

June 25, 1966

US Army Edgewood Arsenal  
Edgewood Arsenal, Maryland 21010

Contract DA-18-035-AMC-715(A)  
Task 1C622104A10204

Department of Chemistry  
THE UNIVERSITY OF TEXAS  
Austin, Texas

DDC  
SEP 27 1966  
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## FOREWORD

The work described in this report was authorized under Task 1C622104A10204, Detection and Warning techniques (U). The work reported herein was started on December 16, 1965. The experimental data are contained in chemistry department record books KSV-3 and BC-2.

## Acknowledgements

The authors are indebted to L. O. Wheeler for aid in running and interpreting the e. s. r. spectra.

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## DIGEST

The electrochemical oxidation of tributylphosphine in dimethylformamide solution containing sodium perchlorate as supporting electrolyte occurs at very positive potentials. A mechanism is proposed for this reaction which involves an initial one-electron abstraction followed by parallel catalytic and kinetic reactions.

The electroreduction of tris-(p-nitrophenyl)phosphate has been studied by polarography, cyclic voltammetry, coulometry, and e. s. r. A mechanism for the reduction based on an initial two-electron reduction step, followed by cleavage to form 4,4'-dinitrobiphenyl, is proposed.

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# FUNDAMENTAL STUDIES IN ELECTROCHEMISTRY

by

Bruce Campbell, K. S. V. Santhanam and Allen J. Bard

## INTRODUCTION

The results of the initial survey of compounds suggested that many organophosphorous are electroactive in nonaqueous solvents. We now decided to do detailed studies on individual classes of compounds, starting with the phosphines, and continuing with the phosphine oxides, phosphites, phosphonates, phosphates, etc. In this report the results obtained with tributylphosphine, and a proposed mechanism for the oxidation of this compound is reported. The study of the electrochemical reduction of tris-(p-nitrophenyl)phosphate has been completed and the results are also reported here.

## EXPERIMENTAL

The general experimental methods and purification techniques are the same as those in the previous report.

A multipurpose instrument employing operational amplifier circuitry with a three electrode configuration<sup>(1)</sup> was used in the voltammetric experiments. Controlled potential coulometry was carried out using a previously described apparatus<sup>(2)</sup>. Cyclic polarograms were run at a platinum disk electrode (area = 0.031 cm<sup>2</sup>). The reference electrode was an aqueous S. C. E. connected via an agar plug and sintered glass disk to a salt bridge containing the test solution and closed at the end by a fine porosity sintered glass disk. A platinum gauze electrode was used in controlled potential experiments. The auxiliary electrode was silver. The e. s. r. spectra were obtained with a Varian Associates V4502

spectrometer employing 100 KC field modulation. A Varian V-153C klystron (output 300 MW) was used; attenuation levels represent attenuation of the output of this klystron in a standard Varian bridge. Samples were contained in the flat Varian aqueous cell. Calculations were performed on a Control Data Corporation 1604 computer. Theoretical simulated spectra were plotted on a CDC 160 plotter.

Tris-(p-nitrophenyl)phosphate (TNP) was obtained from Aldrich Chemical Company and was used without further purification. 4-Nitrophenylphosphate was prepared by passing an aqueous solution of the sodium salt through a cation exchange resin column and recrystallizing it twice from water (m. p. 105 - 107°C). Other nitro compounds were obtained from Aldrich and used without further purification. Tetra-n-butylammonium iodide (TBAI) was polarographic grade, obtained from South Western Analytical Chemicals (Austin, Texas). Tributylphosphine (TBP), obtained from Carlisle Chemical Works, was redistilled and stored under nitrogen.

The experimental procedures for the polarography, cyclic voltammetry and controlled potential coulometry on the vacuum line have been described<sup>(3)</sup>.

## RESULTS AND DISCUSSION

### ELECTROCHEMICAL OXIDATION OF TRIBUTYLPHOSPHINE

#### Cyclic Voltammetry

In the system sodium perchlorate-dimethylformamide, cyclic voltammetry shows an electrochemical oxidation of tributylphosphine (TBP) near +1.35 V. At concentrations of 5mM or less and scan rates of 0.01 to 1 V./sec, the observed oxidation wave is low and merges with the background to an extent that meaningful data are not obtainable. Higher concentrations and fast scan rates are necessary to show a definite peak (Fig. 1). Even under these conditions the peak still merges with the background and the currents are very large; both of these difficulties prevent accurate determination of



peak potentials and peak currents. Even with concentrated solutions and fast scan rates (up to 12.6 V./sec) a reverse reduction peak at potentials near that of the original oxidation is not observed. A reduction peak is observed, but with a peak potential of -0.385 V. This reduction is also seen after exhaustive oxidation. After coulometric oxidation the reduction peak mentioned above and an associated oxidation peak are observed; peak potential values for these are listed in Table 1. No reduction peak is observed for an initial reduction scan.

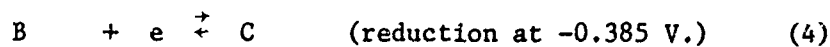
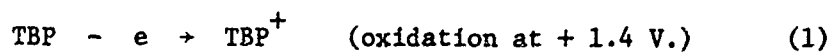
#### Controlled Potential Coulometry

Coulometric oxidation of TBP shows a dependence of the apparent number of electrons ( $n_{app}$ ) with the initial concentration of TBP (Table 2). The current decay, plotted as log current vs. time, (Fig. 2) was not a straight line, but did decay to background after an electrolysis time of forty minutes or longer.

After exhaustive oxidation, coulometric reduction of the reducible species seen with cyclic voltammetry was performed. The values of  $n_{app}$  obtained were slightly less than three, but no variation with concentration was noted. The current fell quickly to background and no dependence of  $n_{app}$  on time between coulometric oxidation and coulometric reduction was observed. During the course of the electrolysis gas evolution was noted.

#### Proposed Mechanism

The following mechanism fits the observed experimental results:



The first three steps are based on the observation that  $n_{app}$  for coulometry approaches one as the concentration is lowered and that the log current vs. time graph is curved. This curvature suggests either a regeneration of the original oxidizable species (catalytic reaction) or the production of another substance that is oxidizable at the oxidation potential used. Since the current did eventually reach the background level, the catalytic reaction or the production of a new oxidizable species would have to be part of a two path reaction; the second path is the removal of any of one of the species involved in the oxidation.

A comparison of graphs of  $n_{app}$  vs. initial concentration of TBP with the theoretical curve obtained by Geske and Bard, case IIIc<sup>(4)</sup> allows an estimate of the order of kinetic reactions occurring and a ratio of the catalytic rate constant to that of the other reaction path. This estimate is that a second order catalytic reaction (reaction 2) and a first (or pseudo-first) order reaction with a ratio of rate constants of about 0.1 are occurring. A lower limit for the rate constant of reaction 3 was calculated to be about  $7 \text{ sec}^{-1}$ . This value was obtained from cyclic voltammetric data in the following manner. The voltammogram with a scan rate of 12.6 V./sec was examined, and the ratio of the initial oxidation peak current to that of the subsequent reduction peak was found to be about 1. Since the reduction is reversible and involves the exchange of one electron (see below) and the initial oxidation involves one electron, as shown by coulometry, the concentrations of the species giving rise to these two peaks were approximately equal. With the assumption that at least two half lives must have occurred from the time of oxidation to the time of the appearance of the reduction peak, and at the scan rate employed a lower limit of the rate constant could be set. This also puts an approximate lower limit for the catalytic reaction, as about  $0.7 \text{ sec}^{-1}$ . More accurate determination of the rate constants is being undertaken by means of potential-step electrolysis. Investigation of the solution after coulometric oxidation by electron spin resonance spectroscopy did not reveal the presence of any stable free radical.

The new species (B) formed by reaction of  $\text{TBP}^+$  in (3) appears to be stable in solution, since, as mentioned above, no time dependence was noted

between the end of the coulometric oxidation and the coulometric reduction. The reduction peak seen by cyclic voltammetry has a peak potential separation of 54 mV. from the peak potential of the re-oxidation process. This suggests a one electron, reversible, reduction, since the theoretical value for a reversible one-electron exchange is about 58 mV. Since the reduction is followed by a chemical reaction, there is a difference in the cathodic and anodic peak current magnitudes. This difference in peak currents allows a calculation of the rate constant of the following reaction, using the treatment of Nicholson and Shain (5) (case VI). The rate constant obtained from the ratio of peak currents was slightly below  $0.1 \text{ sec}^{-1}$ . The value obtained from peak potential shifts with scan rate was also about  $0.1 \text{ sec}^{-1}$ . The reaction following reduction is probably responsible for the gas evolution seen in coulometry.

The coulometric  $n_{\text{app}}$  of three for the reduction is the basis for the postulated last step (reaction 6). Since cyclic voltammetry has shown a one electron reduction with a following reaction, the new species produced by this following reaction must be reduced in a reaction involving electrons. The presence of a species such as D is also seen in cyclic voltammetry using fast repeated scans, when a peak near a potential of  $-0.5 \text{ V}$  is observed. No further information has been obtained for this step.

Tributyl phosphine oxide (TBPO) was briefly investigated with cyclic voltammetry and found to be reduced at a potential of  $-2.3 \text{ V}$ . on mercury in a  $\text{TBAClO}_4$ -dimethylformamide solution. The electrochemical evidence shows that tributyl phosphine oxide is not involved in the electrochemical reactions of tributyl phosphine as performed here.

Further investigation of the various intermediate species is being undertaken to substantiate and elucidate the proposed mechanism.

#### THE ELECTROREDUCTION OF TRIS-(P-NITROPHENYL) PHOSPHATE

Tris-(p-nitrophenyl)phosphate (TNP) was chosen as a model compound for studies of organophosphorous electrochemistry because of the well-known and

usually well-defined behavior of organic nitro-compounds in nonaqueous solutions. (6, 7)

#### Voltammetric Methods

Polarograms of TNP in N, N dimethylformamide solution containing 0.1M tetra-n-butyl ammonium iodide (TBAI) showed five waves (Figure 3); a prewave followed at more negative potentials by one well-defined and three ill-defined waves. The halfwave potentials ( $E_{1/2}$ ) of these waves are -0.83V, -1.7V, -1.9, -2.2 and -2.5V. vs. an aqueous saturated calomel electrode (S. C. E.). The value of  $E_{3/4} - E_{1/4}$  for the well-defined wave (wave 2) (Tómes criterion for reversibility), 0.08V., suggested an irreversible reduction. The wave height of the prewave varied directly with the height of the dropping mercury electrode (D. M. E.), which is characteristic of the adsorption controlled process. The diffusion current of the well-defined wave varied as the square root of the head of the D. M. E. The diffusion current of the third wave was independent of the head of the D. M. E. indicating an electrode reaction involving a preceding chemical reaction (a "kinetic" current). Measurements on the third and fourth waves were difficult to make because of the occurrence of maxima. In order to estimate the number of electrons involved in wave 2 from the Ilkovic equation, an estimate of the diffusion coefficient of TNP is required. The diffusion coefficient of triphenyl phosphate is about  $6.79 \times 10^{-6} \text{ cm}^2/\text{sec}$ , when calculated using the Stokes - Einstein equation using a density of triphenyl phosphate<sup>(8)</sup> of 1.202. The use of this value of D in the Ilkovic equation, with experimental values of  $i_d$ , m, and t, indicates that the main reduction process (wave 2) involves about two electrons (1.97).

A cyclic voltammogram of TNP in DMF containing 0.1M TBAI, at a platinum electrode is shown in Figure 4, curve 1. While essentially same results were obtained with a hanging mercury drop electrode (HMDE), stirring phenomenon<sup>(3)</sup> complicates the measurements of peak currents and potentials. The shape and position of the prepeak was dependent on the scan rate, shifting to more negative potentials with an increase in scan rate and tending to merge with the main peak. The effect of scan rate

on the main process (wave 2) is to shift the peak potential to more negative potentials with increasing scan rate, a shift of 30 mv for a tenfold change in the scan rate. This test of Nicholson and Shain (5) indicates the reduction process is irreversible. A clear anodic peak on the reverse scan with the difference between cathodic and anodic peak potentials of more than 100 mv suggests that this irreversibility is caused by a chemical reaction following the cathodic charge transfer. The results are shown in Table 3.

If the scan is continued past the second peak (Figure 4, Curve 2), three other cathodic peaks appear on the cyclic voltammogram. Data for these peaks are also given in Table 3. The current function (proportional to  $i_p/v^{1/2}$ ) for the second and third peaks decreased, while the current function and for the fourth peak increased substantially, as the scan rate increased. These data, compared with the diagnostic criteria reported by Nicholson and Shain<sup>(9)</sup>, suggest that TNP is involved in an ECE-type reaction with the species produced by the intervening chemical reaction being reduced as or more easily than TNP. The large increase in the current function in peak 4 (as compared to changes in peaks 2 and 3) probably is due to a higher number of electrons involved in that electrochemical process. The data suggest that the third and fifth peaks in cyclic voltammetry and the third and fifth wave in polarography can be ascribed to the reduction of products of the chemical reaction.

#### Controlled Potential Coulometry

Coulometric experiments at a platinum gauze electrode at a potential on the diffusion plateau on the second wave (-1.30V vs. S. C. E.) were undertaken to examine the nature of the reduction products. The reduction of TNP consumed four faradays of electricity per mole. Electrolysis products were examined by cyclic voltammetry and electron spin resonance spectrometry (e. s. r.).

The cyclic voltammetry of the reduced solution is shown in Figure 4, Curve 3. On an initial cathodic scan, a peak at -1.96V. vs. S. C. E., with a corresponding anodic peak on reversal appeared. Cathodic current function

for their wave was fairly constant suggesting that the process is diffusion controlled.

Controlled potential oxidation of the reduced solution at  $-0.80$  V vs. S. C. E. yielded a cyclic voltammogram with peaks at  $-1.06$ V,  $-1.36$ V,  $-1.96$ V and  $-2.47$ V vs. S. C. E. (Fig. 4, Curve 4). The later two peaks were also present in the reduced solution. If no complications due to chemical reaction were present, controlled potential oxidation would lead to the original cyclic voltammogram. The appearance of new peaks on coulometric reduction and oxidation indicate the presence of new systems due to chemical reaction. To determine the identity of the various intermediates in the electroreduction of TNP, a comparison of peak potentials with those of various known nitro-compounds (Table 4) was made. Dinitrobiphenyl appears to be one of the products of chemical reaction. The other product could not be identified definitely by potentials alone but it appears to be a system closely related to 4-nitrophenylphosphate.

#### Electron Spin Resonance

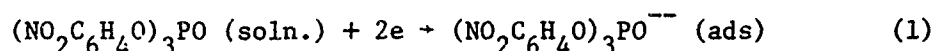
The e. s. r. spectrum of the solution obtained after coulometric reduction was 35 gauss wide and not fully resolved (Figure 5). The variation of relative intensities of lines in the middle and on the outside of the spectrum with varying klystron power levels suggested that this spectrum was caused by two different radicals. During continuous observation, the wide spectrum changed into one that was 16 gauss wide and fully resolved at low power levels. (See Figure 6 a). However, at usual power levels, saturation of this spectrum occurred and only thirteen broad lines were observed.

The second experimental spectrum (Figure 6 a) appears to be that of 4,4'-dinitrobiphenyl anion radical, and it can be interpreted with the following coupling constants:  $a_N = 2.61g$ ,  $a_H = 1.18g$ , and  $a_A = 0.20g$ . (See Figure 6 b). The ESR spectrum of 4,4'-dinitrobiphenyl has been reported with  $a_N = 2.69$ ,  $a_H = 1.23$ , and  $a_H = 0.20$ <sup>(10)</sup>. Using these coupling constants and our experimental conditions of scan rate and linewidth, this spectrum was reproduced by computer for comparison. (See Figure 6 c).

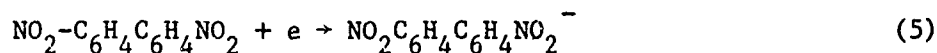
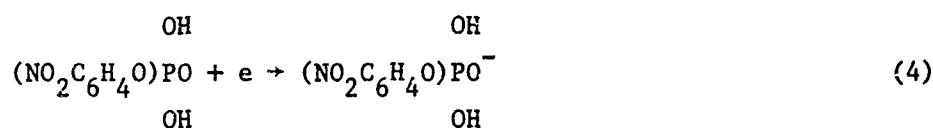
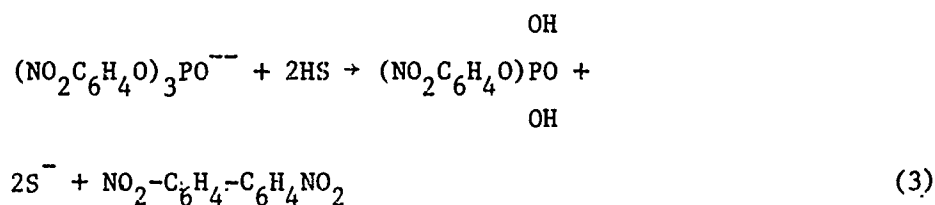
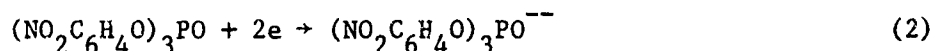
On the basis of this data, it was proposed that the solution as obtained by coulometry contained a mixture of two radicals, one of which was 4,4'-dinitrophenyl anion radical and the other being nitrophenyl phosphate anion radical. The latter radical is more unstable and rapidly decayed leaving the 4,4'-dinitrophenyl.

#### Proposed Mechanism

Although the reaction appears to be quite complicated, the following mechanism appears to be consistent with the electrochemical and e. s. r. results. The first wave is probably an adsorption prewave such as



or it might involve reduction of adsorbed TNP. The polarographic data indicate that wave 2 is a two electron reduction and the cyclic voltammetric data suggests an ECE mechanism such as



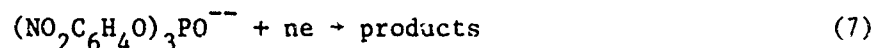
where HS is the solvent and all of these reactions occur at potentials near those of wave 2; reaction 4 occurs at potentials just a little more negative than that of reaction 2 and could barely be noticed as a small separate wave in cyclic voltammetry. Reaction 5 occurs at potentials more positive

than that of reaction 2. During polarography, during the short lifetime of the drop (.3 secs), reaction 3 does not progress to a very large extent, and wave 2 is close to a two-electron reduction wave. During coulometric reduction, which occurs over about 30 minutes, reaction 3 goes essentially to completion, and four electrons per molecule of TNP are consumed. This scheme also accounts for the e. s. r. results.

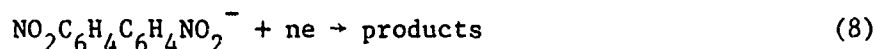
Since the current function of wave 3 decreases with increasing scan rates, it is probably due to reaction of a product of reaction 3, such as



On the other hand, the current function of wave 4 increases with increasing scan rate, and can be ascribed to



Wave 5 can be ascribed to a reaction such as



since 4,4'-dinitrobiphenyl has a reduction wave at these potentials (Table 4).

The formation of 4,4'-dinitrobiphenyl indicates that reaction occurs by the cleavage of the oxygen - carbon bond, while the energy rich phosphorous - oxygen bond remains intact. A similar cleavage of oxygen - carbon has been proposed by Mittel<sup>(11)</sup> in the reduction of diphenyl phosphate. Our results differ from these in that we did not observe nitrobenzene as the cleavage product; nitrobenzene peak potentials are given in Table 4.

The question arises from the e. s. r. studies as to the mode of decay of nitrophenylphosphate-like radical in the mixture. If oxygen were to



diffuse slowly into the e. s. r. cell, the peak potentials for oxygen and nitrophenyl phosphate reduction are  $-1.07V^{(12)}$  and  $-1.36V$  vs. S. C. E., respectively, so that radical could reduce oxygen. However, the reaction between 4-4'-dinitrobiphenyl anion radical, peak potential of  $-0.93V$  vs. S. C. E., and oxygen is less likely.

#### CONCLUSIONS

The electrochemical oxidation of tributylphosphine in dimethylformamide solution containing sodium perchlorate as supporting electrolyte occurs at very positive potentials. A mechanism is proposed for this reaction which involves an initial one-electron abstraction followed by parallel catalytic and kinetic reactions.

The electroreduction of tris-(p-nitrophenyl)phosphate has been studied by polarography, cyclic voltammetry, coulometry, and e. s. r. A mechanism for the reduction based on an initial two-electron reduction step, followed by cleavage to form 4,4'-dinitrobiphenyl, is proposed.

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APPENDIX I

Table 1. CYCLIC VOLTAMMETRIC DATA OF TBP AFTER  
COULOMETRIC OXIDATION AT + 1.38 V

The concentration of TBP was 2.0 mM in 0.1 M NaClO<sub>4</sub> - DMF. The electrode area was 0.018 cm<sup>2</sup>. Potentials vs. aqueous S. C. E. ———

<u>Sweep Rate</u>	<u>Reduction Peak</u>		<u>Oxidation Peak</u>	
	<u>E<sub>p</sub></u>	<u>i<sub>p</sub></u>	<u>E<sub>p</sub></u>	<u>i<sub>p</sub></u>
<u>V/sec</u>	<u>V</u>	<u>μa</u>	<u>V</u>	<u>μa</u>
0.255	-0.385	34	-0.333	24
0.189	-0.385	31	-0.329	18
0.119	-0.385	24	-0.331	16
0.0579	-0.385	17	-0.331	10
0.0342	-0.385	13	-0.331	9
0.0119	-0.385	8	-0.331	6

Table 2. APPARENT NUMBER OF FARADAYS PER MOLE  
FOR COULOMETRIC OXIDATION OF TBP

Oxidation at Pt gauze anode at + 1.38 V. vs. S. C. E.

<u>n<sub>app</sub></u>	<u>Initial Concentration of TBP (mM)</u>
2.55	4.76
1.55	2.0
1.15	1.1

Table 3. CYCLIC VOLTAMMETRIC DATA FOR REDUCTION OF TRIS P-NITROPHENYL PHOSPHATE

The solution contained 0.1 M TBAI and 2.85 mM TNP in DMF. The working electrode was a Pt disk electrode, 0.031 cm<sup>2</sup>. Potentials vs. aqueous S. C. E.

Sweep Rate, v, (mV/sec)	Peak 2		Peak 3		Peak 4		Peak 5	
	E <sub>pc</sub>	$\frac{i_p}{v^{1/2}}$	E <sub>pc</sub>	$\frac{i_p}{v^{1/2}}$	E <sub>pc</sub>	$\frac{i_p}{v^{1/2}}$	E <sub>pc</sub>	$\frac{i_p}{v^{1/2}}$
(V.)			V		V		V	
67.1	-1.13	3.27	-1.96	3.12	-2.24	0.81	-2.51	6.11
153	-1.14	3.08	-1.96	2.27	-2.30	2.01	-2.55	3.39
222	-1.14	2.96	-1.99	1.93	-2.34	2.47	-2.59	1.98
312	-1.15	2.97	-1.99	1.24	-2.34	2.91	-2.61	—
476	-1.15	2.94	-2.00	0.91	-2.41	3.27	—	—
712	-1.16	2.96	-2.01	0.75	-2.49	3.27	—	—

\* in  $\mu\text{a-sec}^{1/2}$ - $\text{mv}^{-1/2}$

Table 4 CYCLIC VOLTAMMETRIC DATA FOR  
REDUCTION OF NITRO COMPOUNDS

The solution contained 0.1 M TBAI and 2.85 mM TNP in DMF. The working electrode was a Pt disk electrode, 0.031 cm<sup>2</sup>. Potentials vs. aqueous S. C. E.

Compound	E <sub>pc</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>pa</sub>	E <sub>pc</sub>	E <sub>pc</sub>
Tris p-nitrophenyl-phosphate	-1.14	-1.01	-1.96	-1.86	-2.24	-2.51
Tris p-nitrophenyl-phosphate (reduced)		-0.93 -1.17	-1.96	-1.86		-2.51
Tris p-nitrophenyl-phosphate reduced and oxidized	-1.06 -1.36	-0.92 -1.17	-1.96	-1.86		-2.47
4-Nitrophenylphosphate	-1.28		-2.02	-1.86		
4,4'-Dinitrobiphenyl	-1.05	-0.90				-2.50*
Nitrobenzene	-1.31	-1.01				

(V. vs. S. C. E.)

\* Broad peak.

APPENDIX II

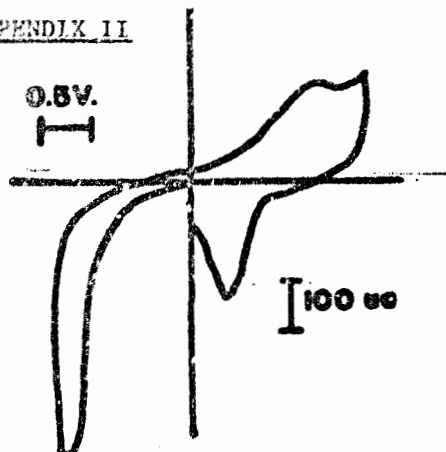


Fig. 1. Cyclic Voltammetry of TBP at platinum electrode. The solution contained 10 mM TBP and the scan rate was 12.6 V/sec.

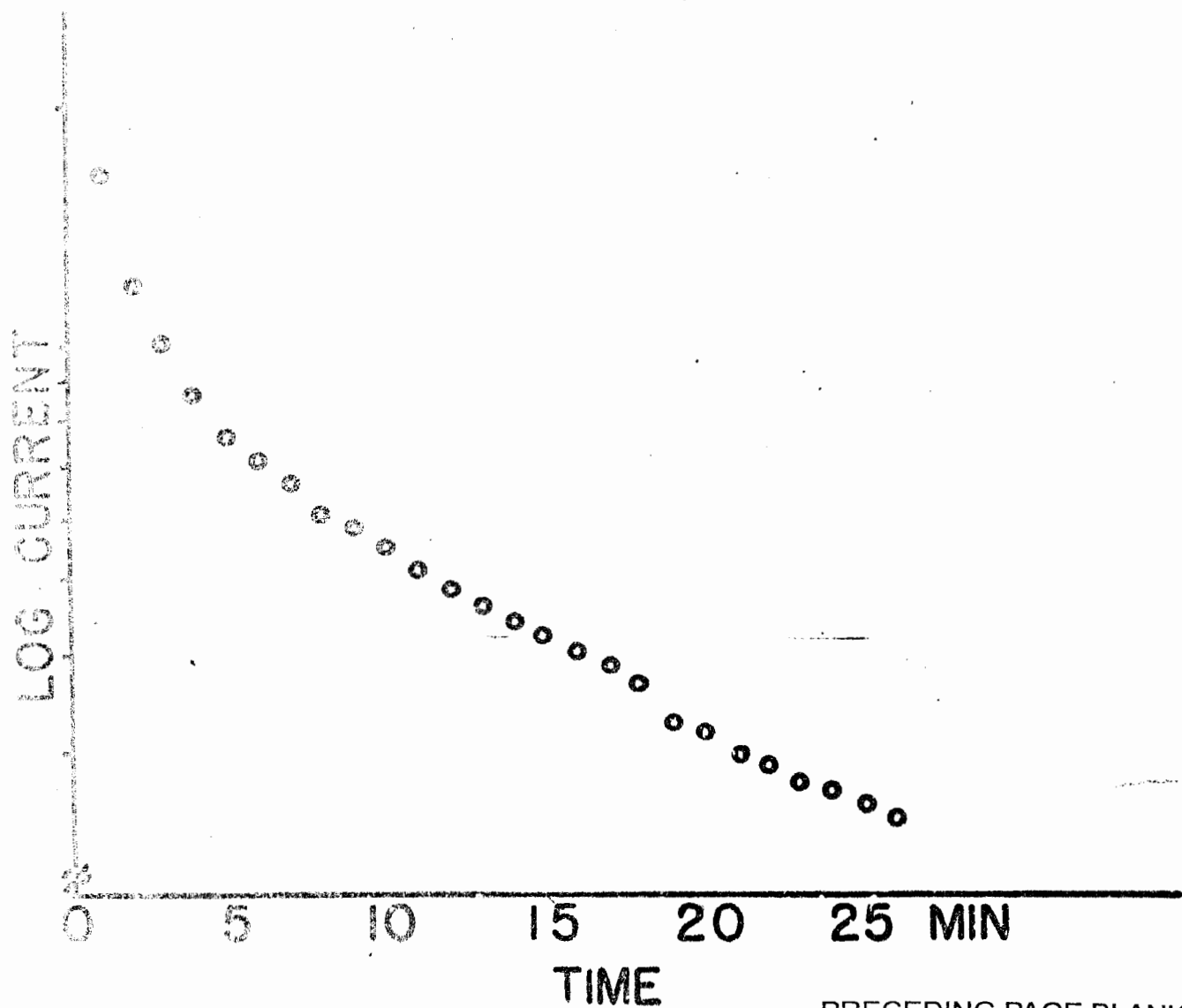


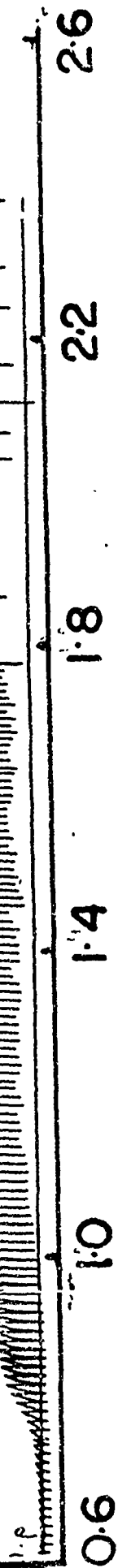
Fig. 2. Current decay during coulometric oxidation of TBP. The initial concentration of TBP was 2.0 mM. Current at 1 minute was 16.1 ma.

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Fig. 3. Polarogram for reduction of Tris-p-nitrophenylphosphate. The solution contained 0.1 M TBAI in DMF with 2.8 mM TNP. Current axis represents 5  $\mu$ a per inch.

CURRENT

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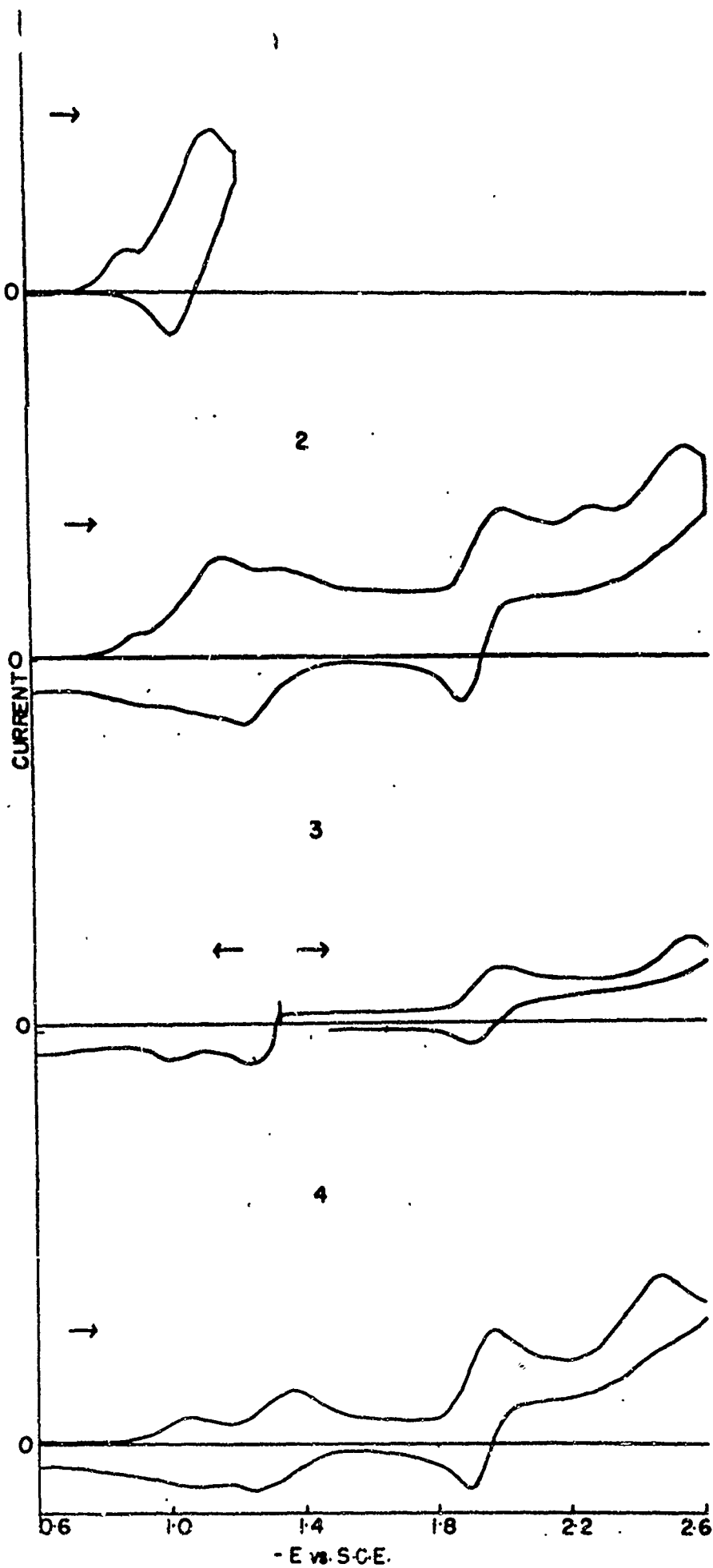


FIG. 15. Top, Derivative ESR spectrum of TNP anion radical produced by electroreduction of 2.8 mM TNP solution containing 0.1 M tetra-n-butylammonium iodide in DMF. Spectrometer conditions: modulation amplitude, 0.05 gauss; power, 18 db, Sweep time, 25 min.  
 Middle: Calculated spectrum using constants in text.  
 Bottom: Calculated spectrum using constants reported by Fraenkel (10).



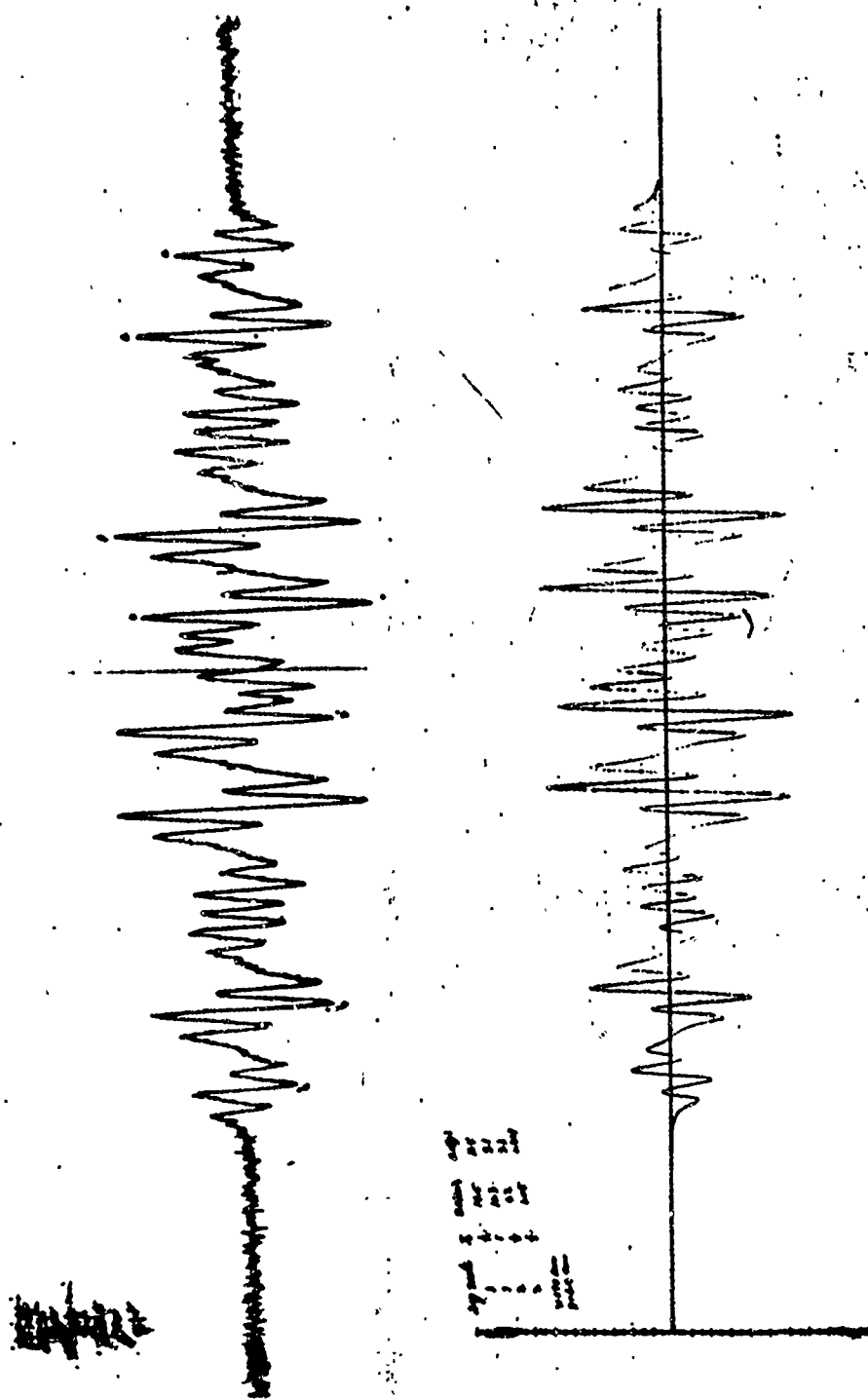


Fig. 2. Top: Derivative spectrum of tris p nitrophenyl phosphate.  
Bottom: Calculated spectrum.

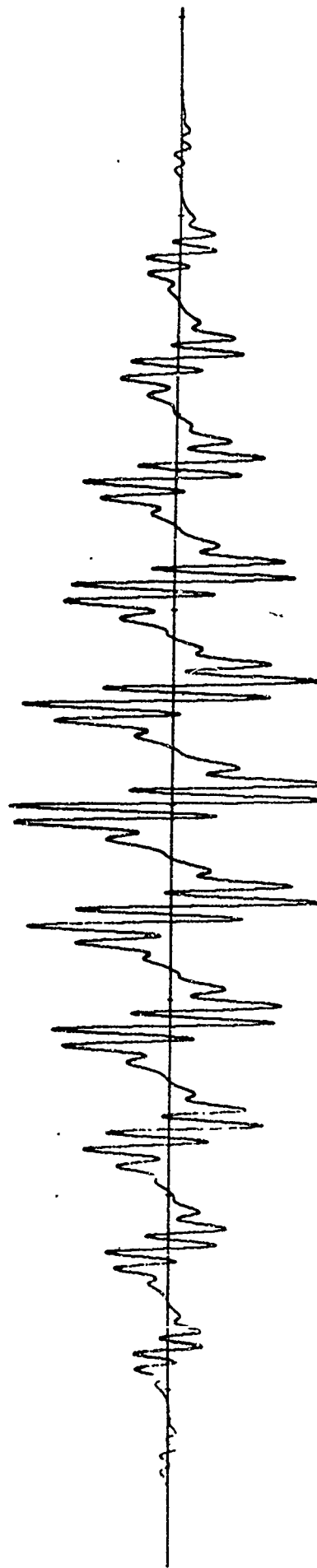
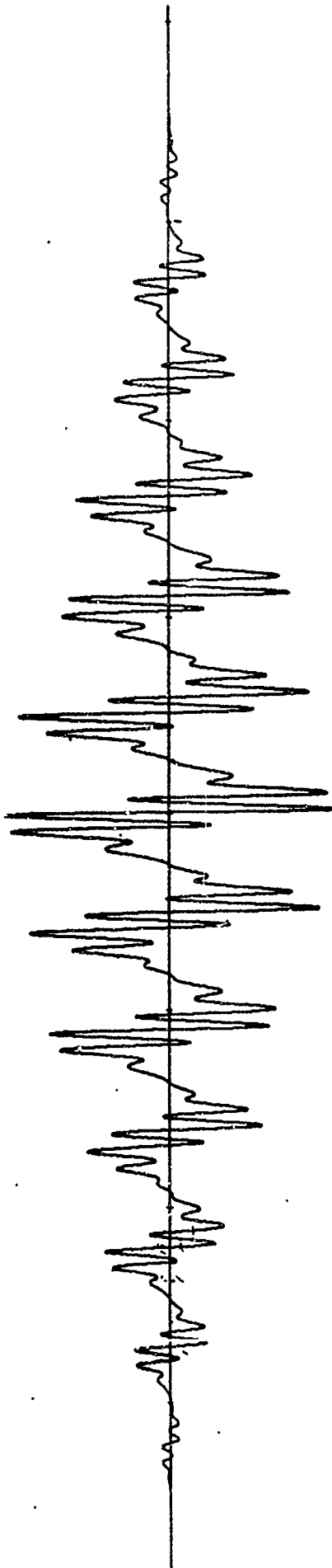
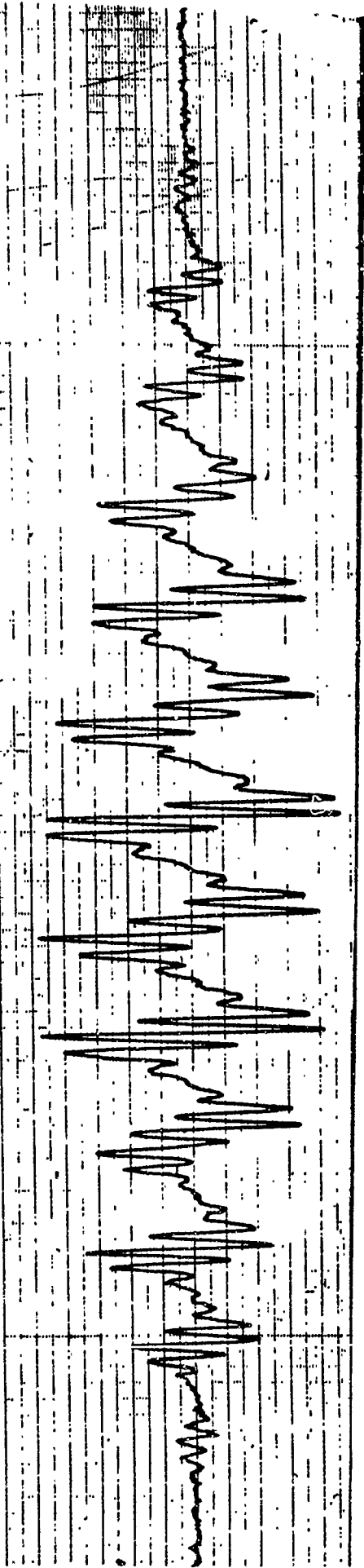


Fig. 5. Cyclic voltammetry of Tris-pnitrophenylphosphate. The solution contained 0.1 M TBAI in DMF and (1) TNP before reduction when the scan is reversed at first peak. (2) Reduction of TNP past the first peak; (3) TNP after reduction; (4) after oxidation of the reduced species.

**UNCLASSIFIED**

Security Classification

**DOCUMENT CONTROL DATA - R&D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

<b>1. ORIGINATING ACTIVITY (Corporate author)</b> Department of Chemistry The University of Texas Austin, Texas		<b>2a. REPORT SECURITY CLASSIFICATION</b> Unclassified	
		<b>2b. GROUP</b> N/A	
<b>3. REPORT TITLE</b>  FUNDAMENTAL STUDIES IN ELECTROCHEMISTRY			
<b>4. DESCRIPTIVE NOTES (Type of report and inclusive dates)</b> Quarterly Progress Report - March 15, 1966 - June 14, 1966			
<b>5. AUTHOR(S) (Last name, first name, initial)</b>  Campbell, Bruce; Santhanam, K. S. V.; Bard, Allen J.			
<b>6. REPORT DATE</b> 1966		<b>7a. TOTAL NO. OF PAGES</b> 033	<b>7b. NO. OF REFS</b> 012
<b>8a. CONTRACT OR GRANT NO.</b> DA-18-035-AMC-715(A)		<b>8c. ORIGINATOR'S REPORT NUMBER(S)</b>  Report Number 2	
<b>a. PROJECT NO.</b>		<b>8d. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)</b>  N/A	
<b>c. Task No.</b> 1C622401A10204			
<b>d. Work Unit</b>			
<b>10. AVAILABILITY/LIMITATION NOTICES</b> This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of CO, USA Edgewood Arsenal, Attn: SMUEA-TSTI-T, Edgewood Arsenal, Md. 21010.			
<b>11. SUPPLEMENTARY NOTES</b>  Detection and warning investigations		<b>12. SPONSORING MILITARY ACTIVITY</b> Research Laboratories U.S. Army Edgewood Arsenal Edgewood Arsenal, Maryland	
<b>13. ABSTRACT</b>  The electrochemical oxidation of tributylphosphine in dimethylformamide solution containing sodium perchlorate as supporting electrolyte occurs at very positive potentials. A mechanism is proposed for this reaction which involves an initial one-electron abstraction followed by parallel catalytic and kinetic reactions.  The electroreduction of tris-(p-nitrophenyl)phosphate has been studied by polarography, cyclic voltammetry, coulometry, and e. s. r. A mechanism for the reduction based on an initial two-electron reduction step, followed by cleavage to form 4,4'-dinitrobiphenyl, is proposed.			
<b>14. KEY WORDS:</b>  Electrochemistry Organophosphorous compounds Cyclic voltammetry Electron spin resonance			

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1 JAN 64

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