

## Triphenylphosphine Phenylimide 의 전기화학적 환원

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## Electrochemical Reduction of Triphenylphosphine Phenylimide

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**요 약.** Triphenylphosphine phenylimide 의 비수용액에서의 전기화학적 환원반응을 polarography, cyclic voltammetry, controlled-potential coulometry 및 electron spin resonance 법을 써서 고찰하였다. 이 유기인화합물은 one-electron transfer 에 따라서 anion radical 이 형성되나 순간일 뿐이고 protonation 과 재차 one-electron reduction 결과 인과 질소사이의 이중결합이 끊어진다. 그 결과 아닐린이 주요 반응생성물로서 발견되었다. 또 한편 동반하는 화학반응결과 생긴 부산물의 하나인 triphenylphosphine oxide 의 환원결과 인과 페닐사이의 단일결합이 끊어지는 것도 관찰할 수 있었다.

**Abstract.** The electrochemical reduction of triphenylphosphine phenylimide in nonaqueous media has been examined by polarography, cyclic voltammetry, controlled-potential coulometry and electron spin resonance spectroscopy. The reduction of triphenylphosphine phenylimide proceeds by a one-electron transfer to form anion radical which undergoes both protonation and a second one-electron reduction followed by cleavage of the phosphorus-nitrogen double bond. Aniline is a major product. The cleavage of a phosphorus-phenyl bond was also observed after reduction of triphenylphosphine oxide which is one of the major products of the chemical reaction which follow the primary process.

### 1. Introduction

Phosphorus compounds have become increasingly important as intermediates in organic

synthesis and ligands in coordination chemistry. The range of application of phosphorus compounds in modern technology is extremely broad and varied. Since phosphorus is sometimes found in minute quantities often in the form of labile or nonvolatile compounds, the detection, assay, and identification of its compounds require considerable skill, forcing the chemist to

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push his analytical tools to their limits of performance.

Free radical intermediates have frequently been postulated for reactions involving organophosphorus compounds. However, comparatively few phosphorus-containing radicals have been prepared in solution under conditions which permitted their study in detail by *esr*. As early as 1953 Heine and coworkers<sup>1</sup> reported that the reaction of phosphine oxides with alkali metals led to colored, paramagnetic solution; however, a review<sup>2</sup> of the literature of phosphorus *esr* in 1966 counted only 16 publications. Since that time, a number of additional studies have appeared. Cowley<sup>3</sup> has reported several radicals containing phosphorus, Lucken<sup>4</sup> has observed phosphorus radicals in irradiated solids, and several radicals have been detected as an adjunct to the electrochemical studies by Bard and coworkers<sup>5-7</sup>. Recently Matcalfe and Waters<sup>8</sup> have reported the formation of radicals from phosphorus and phosphoric acid esters in a fast flow system and Dimroth<sup>9</sup> has prepared a novel heterocyclic phosphorus radical. The first indication of hindered intramolecular motion in a phosphorus radical has been detected recently by Rieker<sup>10</sup> *via* line-width variations.

From the industrial point of view, triphenylphosphine phenylimide (PPPI) was chosen as phosphorus-nitrogen compound; considerable interest has arisen recently in polymers which have the general formula  $(N=P(OR)_2)_n$ .<sup>11</sup> Some of the desirable properties of these materials have been attributed specifically to the presence of the phosphorus-nitrogen double bond ( $-N=P-$ ) which is, it is pointed out,<sup>11</sup> isoelectronic with the  $-Si-O-$  skeletal unit of the silicon series, and the two units behave similarly in many instances. We have now examined the mechanism of the reduction of PPPI, which is subject of this report.

## 2. Experimental

### 2.1. Chemicals

Acetonitrile and tetraethylammonium perchlorate (TEAP) supporting electrolytes were prepared by standard literature methods.<sup>12</sup> PPPI was prepared by reaction of phenyl azide (in hydrocarbon solution obtained from Pfaltz and Bauer, Inc., Flushing, N. Y.) and triphenylphosphine in ether solution. This reaction is known as Staudinger reaction.<sup>13</sup> After three recrystallizations from *n*-hexane, the resulting crystals melted at 131~131.5° which is in agreement with the melting point reported by Wiegraebe and Bock.<sup>14</sup> Other chemicals were available from standard commercial sources.

### 2.2. Electrochemistry

Polarographic measurements were made with the solid state polarograph, employing operational amplifier circuiting with a three electrode configuration, described previously.<sup>15</sup> For rapid-sweep cyclic voltammetry, a Tektronix type 201-W oscilloscope equipped with type D plug-in amplifiers was employed. Pictures were recorded with an oscilloscope camera and a type 2620 Polaroid attachment. At slow-sweep rates, Moseley model 2D-2M X-Y recorder was used. A Hewlett-Packard model 3300 A function generator with a model 3302 A trigger served as the signal generator. Controlled-potential electrolysis were carried out using a Princeton Applied Research (PAR) model 173 potentiostat equipped with PAR model 177 current readout module. Coulometry was carried out using a nitrogen-hydrogen coulometer as described by Lingane.<sup>16</sup> Additional cyclic voltammetry experiments were carried out using the signal generator and oscilloscope described above in conjunction with the PAR 173. In these experiments, a PAR model 176 current to

voltage converter was used and positive feedback IR compensation was employed.

The electrolysis cell was a three compartment vessel for polarography and cyclic voltammetry. Aqueous saturated calomel electrode(sce) was used as the reference electrode which was isolated from the working electrode compartment by means of a fritted disk, the auxiliary electrode was a platinum wire and a dropping mercury electrode was the working electrode. For cyclic voltammetry, a mercury-coated platinum<sup>17</sup> or a platinum-disk electrode replaced the dropping mercury electrode. The mercury-coated platinum wire electrode was made by sealing platinum wire into a soft-glass tube, as described previously.<sup>18</sup> The auxiliary electrode was a platinum wire and the reference electrode was an aqueous sce. The working electrode in the controlled-potential electrolysis was a mercury pool of approximately 7 cm<sup>2</sup> area which was stirred continuously during the controlled-potential electrolysis. The reference(sce) and auxiliary (mercury pool) electrodes were separated from the working electrode compartment by means of, respectively, a glass fritted disk and a bridge containing solvent and supporting electrolyte between two fritted disks.

**Polarography and Cyclic Voltammetry.** In a typical polarographic experiment, a freshly prepared solution of TEAP (0.1 M) and starting material (ca. 1~4 mM) in acetonitrile (25 ml) was transferred to the electrolysis cell and the three electrodes were introduced. The solution was then purged for 30 minutes with prepurified nitrogen which was passed first over hot copper wool and then through purified acetonitrile. The pre-saturation step minimized loss of solvent from the cell. An atmosphere of nitrogen was then maintained over the solution as the voltammograms were recorded. In a typical cyclic

voltammetric experiment, freshly prepared solutions were used, identical with those employed in polarography. The same cell as used for polarography was employed except for the use of a mercury-coated platinum wire or platinum disk working electrode. After each solution was purged with nitrogen the potential range was swept back and forth by means of the triangle wave generator connected to the summing point of the control amplifier in the polarograph. The frequency range of 0.01~10 cps was usually investigated, with the voltammograms being recorded either on X-Y recorder (>1 cps) or by photography from the oscilloscope for the higher sweep rates. The precision of potentials measured from chart recording is estimated at the  $\pm 5$  mV level. Larger uncertainties, estimated at 5% were encountered in oscilloscopic measurements.

**Controlled-potential Electrolysis.** When coulometric measurements were made, cathodically reactive impurities were destroyed by pre-electrolysis; a measured volume (usually 25 ml) of background solution (0.1 M TEAP-MeCN) was introduced into the working electrode compartment of a three compartment cell. This solution was electrolyzed at the potential which was employed for the controlled-potential electrolysis of the compound until a steady-state current was reached. After pre-electrolysis, a weighed amount of the sample sufficient to make the solution ca. 1~4 mM was introduced into the working electrode compartment. After dissolution, electrolysis was recommenced at the same potential, stirring rate and flow rate of nitrogen. The temperature was not controlled. However, cell heating was not observed to any great extent. Completion of electrolysis was confirmed by obtaining a steady-state current.

### 2.3. Product Analysis

Analysis of electrolysis products were carried out using gas chromatography, voltammetry and thin-layer chromatography (TLC) followed by spectroscopic methods. The gas chromatograph was a Perkin-Elmer model 990 equipped with thermal conductivity detector. The infrared spectra were taken on either model 21 or model 257 Perkin-Elmer spectrometers, using standard techniques; the ultraviolet spectra were recorded on a Cary model 14 using quartz cells; the NMR spectra were determined either on a Varian model A 60 or 90 MHz Bruker model H FX-10 spectrometer; the low resolution mass spectra were taken on a Nuclide instrument; the high resolution mass spectra were taken on an Associated Electronics Industries MS 902 instrument equipped with a computer for data reduction and elemental analysis printout.

Small analytical TLC plates were prepared by dipping microscope slides in a slurry of silica gel containing an inorganic fluorescent indicator and gypsum (Merck GF-254) in 2:1 chloroform and methanol. Preparative plates were prepared by coating 20 × 30 cm glass plates with aqueous slurry of silica gel GF-254 (60 g silica gel-120 ml water-shake for about 30 seconds-enough for two plates). The wet plates were air-dried for overnight and were then activated in oven at 105° for 2 hours. The base line was fixed at a distance of 20 mm from the edge of the plates, and a benzene extract of the electrolysis products was applied to the plates. The chromatograms were developed in one-dimension (by the ascending method) in a glass tank containing solvent mixture. After the plates were removed from the developing chamber they were air-dried and the dry gel of each zone was scraped from the plates and was placed on a column, the bottom of which had been plugged with a sintered glass frit. The gel of each zone was then eluted with solvent. The

solvent was evaporated from each eluant under reduced pressure and the resulting material was examined by spectroscopic methods.

**Aniline.** After the electrolysis, the catholyte was analyzed without workup by gas chromatography using 4.0 ft column containing 5.0 % diethylene glycol succinate on Chromosorb W at 125° with a helium flow rate of 50 ml/min. Aniline was eluted with a retention time of 5.0 minutes. Standard solutions containing 100 mg of aniline in 25.00 ml of acetonitrile was prepared and aliquots of these standard solutions were employed to obtain analytical curves. The respective peak height was plotted against the weight of aniline in the standard solution. In order to investigate further evidence for aniline the following experiments were carried out. The GC effluent was trapped from the exit port of the gas chromatograph in a melting point tube cooled with liquid nitrogen. The trapped effluent was examined by UV, IR, and NMR spectroscopic experiments.

**Triphenylphosphine (TPP) and Triphenylphosphine Oxide (TPPO).** After the electrolysis acetonitrile was removed from the catholyte by evaporation under reduced pressure and the remaining residue was extracted with benzene. The benzene extract was analyzed by thin-layer chromatography. Development of the plates with a solvent mixture (benzene-acetone, 75/25) was carried out by the ascending method and led to the formation of four separate zones. After the plates were removed from the developing chamber, the two zones of dry gel ( $R_f$  values of 0.40 and 0.82) were scraped, respectively, from the plates and then eluted with chloroform. The solvent was evaporated from each eluant and the resulting residue was examined by UV, IR and NMR spectroscopic methods. Quantitative estimations of these compounds were performed as follows. A known

amount (100~200  $\mu$ l) of the benzene solutions was placed on the preparative plates. After development of the plates with the solvent mixture described above the two zones of dry gel were scraped, respectively, from the plates and then leached from the silica gel with chloroform. The chloroform was evaporated from each eluent and the remaining residue was extracted with acetonitrile. The acetonitrile solution was analyzed by UV absorption spectrophotometry.

**Diphenylphosphinic Acid.** The product solution was evaporated under reduced pressure and was then extracted with benzene. The resulting residue was treated with hot distilled water. Cooling this solution caused precipitation of the supporting electrolyte which was filtered out. The aqueous solution was extracted with ether. The aqueous portion from which ether solution was separated was acidified with 2.0 M hydrochloric acid and extracted with benzene. The benzene solution, after reduced pressure evaporation, gave a white solid which melted at 189~190° which is in agreement with the melting point of an authentic sample of diphenylphosphinic acid. The resulting white solid was then examined by TLC, UV, IR, NMR and mass spectroscopic methods. The white solid was identified as diphenylphosphinic acid by the results of TLC and spectroscopic examinations. Quantitative analysis for diphenylphosphinic acid were carried out by dissolving the white solid in methanol and measurement of the UV spectrum.

**Benzene.** Benzene analyses were performed by gas chromatography of the product solution drawn from the catholyte compartment. A  $3' \times \frac{1}{4}''$  column packed with Porapak Q at 195° with a helium flow rate of 20 ml/min indicated the presence of benzene with a retention time of 10 minutes. Additional evidence for benzene was

obtained by UV absorption spectrophotometry.

In the analysis of the catholyte for aniline by gas chromatography, the appearance of an additional peak with retention time of 7.2 minutes was discovered. In order to investigate the nature of this peak, the GC effluent was trapped and was found to be a very hygroscopic, white crystalline solid, melting point 75°. The isolated white solid was examined by UV, IR, NMR and mass spectroscopic methods in an effort to elucidate the structure.

#### 2.4. Water Analyses

Water concentration in acetonitrile was analyzed by gas chromatography on a 3.0 ft Porapak Q column at 200° with a helium flow rate of 20 ml/min and a retention time of 0.6 minutes. Calibration curves were obtained from mixture of acetonitrile and water; the water content of the solvent was determined by the method of standard additions.

#### 2.5. ESR Spectroscopy

ESR spectra were recorded using a Varian E-12 spectrometer system and the intra muros<sup>19</sup> electrolytic technique of free radical generation.

### 3. Results and Discussion

#### 3.1. Polarography and Cyclic Voltammetry

The polarographic reduction of PPPI in acetonitrile solution containing 0.1 M TEAP showed two waves; one well-defined and the second ill-defined, with half-wave potentials of -2.50 and -2.66 V vs. sce. The variation of the limiting current with the mercury head applied to the dropping mercury electrode was studied for the first wave. As shown in Table 1 the wave height varied approximately with the square root of the mercury head. This behavior suggests that the wave is result of diffusion-controlled process. The value of  $E_{3/4} - E_{1/4}$  for the first wave, -17 mV, suggests an irreversible reduction.

Triangular sweep cyclic voltammetry of 1.0 mM PPPI in 0.1 M TEAP—MeCN solution at a mercury-coated platinum wire cathode yielded one reduction peak with peak potential,  $E_p = -2.65$  V vs. sce. No anodic peak corresponding to the oxidation of the product of the cathodic process was observed on the reversal of the scan at any sweep rate or any switching potential, suggesting a totally irreversible process. From the experimental point of view, a cathodic ece (electron transfer—chemical reaction—electron transfer) system can be classified according to the number of cathodic and anodic waves which are observed. Further classification according to the reversibility or irreversibility of the two charge transfers can be made by examination of the anodic waves as scan rate is varied, since anodic waves are never observed for irreversible charge transfers<sup>20</sup>. From examination of cyclic voltammograms as a function of sweep rate from 0.06 to 0.60 volts per sec using X—Y recording, the current function (proportional to  $i_p/v^{1/2}$ ) is found to decrease as the sweep rate is increased. This fact may indicate a chemical reaction coupled with the electrochemical reaction at these sweep rates (Table 2). The current function is defined as

$i_p/nFA(Da)^{1/2}C^*$ , where  $i_p$  is the peak current,  $v$  is the sweep rate  $C^*$  is the initial concentration of electroactive substance, and the parameter  $a$  is defined as  $a=nFv/RT$ .<sup>21</sup>

### 3.2. Controlled-Potential Coulometry

In view of the isolation of products similar to those produced by hydrolysis of PPPI we verified that hydrolysis does not occur under our experimental conditions. An UV spectrophotometric examination of a solution of PPPI in acetonitrile showed absorption spectra with maxima at 252 and 227 nm, which did not show in the UV absorption spectra of TPPO in

Table 1. Polarographic data<sup>a</sup> for the reduction of TPPI<sup>b</sup>.

Mercury head $h(\text{Corr})$ , cm	$i_d/h^{1/2}$ ( $\mu\text{A}/\text{cm}^{1/2}$ )
91.3	0.37
79.8	0.35
70.1	0.28
61.9	0.27

<sup>a</sup> Data for the first wave.

<sup>b</sup> The solution was 0.1 M TEAP in  $\text{CH}_3\text{CN}$ , and contained 0.69 mM PPPI.

Table 2. Cyclic voltammetric data<sup>a</sup> for the reduction of TPPI in acetonitrile<sup>b</sup>.

Sweep rate $v$ (volts/sec)	Without IR Compensation			With IR Compensation		
	$-E_p$ <sup>c</sup>	$i_{pc}$ <sup>d</sup>	$i_{pc}/v^{1/2}$ <sup>e</sup>	$-E_p$ <sup>c</sup>	$i_{pc}$ <sup>d</sup>	$i_{pc}/v^{1/2}$ <sup>e</sup>
0.06	2.68	75.0	307.4	2.68	80.0	327.9
0.12	2.69	95.0	275.4	2.69	100.0	289.9
0.18	2.71	100.0	237.0	2.71	105.5	250.0
0.24	2.72	110.0	225.4	2.72	115.0	235.7
0.30	2.72	115.0	211.0	2.72	120.0	219.8
0.60	2.73	120.0	155.4	2.73	130.0	168.4

<sup>a</sup> Data for the first sweep. The working electrode was a mercury-coated platinum wire electrode, auxiliary electrode was a platinum wire and aqueous sce was used as a reference electrode; <sup>b</sup> The solution contained 1.40 mM PPPI and 0.1 M TEAP; <sup>c</sup> Volts vs. sce; <sup>d</sup>  $\mu\text{A}$ ; <sup>e</sup>  $\mu\text{A sec}^{1/2}$  Volts<sup>-1/2</sup>

acetonitrile. After letting the solution sit overnight we have found no change in the absorption maxima.

Controlled-potential coulometry of PPPI at a mercury pool cathode on the diffusion current plateau of the first wave at a potential of  $-2.60$  V *vs.* sce was carried out in order to find the number of electrons transferred during reduction of the compound and the nature of the reduction products. Because of the closeness of the background discharge potential ( $-2.85$  V. *vs.* sce), conditions for controlled-potential coulometry are not the most favorable. The most unfavorable factor is, however, the small separation of the two reduction waves;  $E_{1/2}$  of the wave 2 ( $-2.66$  V) is separated by only 60 mV from the cathode potential. As shown in Table 3 the final steady state current in coulometry was approximately 2~8 % of the initial value and also the steady state current is much higher than background value (ca. 0.05 mA). This appears to be due to products which are themselves electroactive at the working electrode potential. In every case, the number of electrons involved in the reduction was found to be approximately four at this potential.

The variation of electrolysis current with time was not exponential. It was found that near the beginning of the electrolysis the current showed nearly a linear decay with time. During the

middle part of the electrolysis the current decreased exponentially eventually reaching a steady state current. These facts suggest that a chemical reaction which follows the charge transfer constantly regenerates an electroactive species. The original colorless solution changed to yellow-orange at the beginning of the electrolysis; then the color turned to yellow during the middle part of the electrolysis. Finally, the solution became colorless again at the end of the electrolysis. All  $\log i$  *vs.* time plots obtained as various concentrations are distinctly non-linear. The curves show concave deviation from linear behavior and their slopes are essentially concentration independent.

The electrochemical behavior of the reduced solution was investigated by means of polarography and cyclic voltammetry. The first cathodic wave has disappeared and the product of the reduction gives rise to a new reduction wave with an  $E_{1/2}$  of  $-2.57$  V. The anodic wave height of approximately 20 % of the cathodic wave corresponds to oxidation of a product of chemical reactions. It was suspected that this new reduction wave was due to the presence of triphenylphosphine oxide. The following procedure was used to confirm the presence of TPPO following the reduction of PPPI. Approximately 1.0 mM solution of TPPO was prepared by addition of authentic TPPO to the reduced

Table 3. Coulometric data for the reduction of TPPI in acetonitrile.

Concn. PPPI (mM)	$i_o$ (mA)	$i_f$ (mA)	$\frac{i_f}{i_o} \times 100$	$n^a$
1.00	12.0	1.05	8.75	4.07
1.71	22.5	1.75	7.78	4.04
1.79	27.0	1.20	4.45	4.01
2.40	43.0	1.05	2.44	3.74
3.35	57.0	1.50	2.63	4.03

<sup>a</sup> Faraday per mole of PPPI.

solution and polarograms were taken under the same conditions. The reduction wave exhibited by the added TPPO occurs at the same potential as the new reduction wave with half-wave potential of  $-2.57$  V and causes an increase in the wave height. This investigation suggested the formation of TPPO in the product solution.

When the reduction was examined by cyclic voltammetry the voltammogram showed three reduction peak potentials at  $-2.13$ ,  $-2.71$  and  $-2.76$  V *vs.* sce. To determine the identity of the new systems, a comparison of the peak potentials with those of various known compounds was made. The reduction potential at  $-2.71$  V agreed well with the TPPO system. The voltammetric data of TPPO showed that the oxide is reducible at the potential employed for controlled-potential coulometry. The reduction of TPPO probably proceeds by a one-electron reduction to the anion radical.<sup>5</sup> Since TPPO was found to be approximately 25% yield from the electrolyzed solution (Table 4), reaction of the anion radical with solvent to regenerate TPPO probably occurs. The nature of the other peaks were not investigated further, but they are assumed to be caused by minor products of undefined side reactions.

After electrolysis, the reduced solution was

examined by UV absorption spectrophotometry. The UV spectrum consists of three sharp intense peaks at 272, 265 and 222 nm. Comparison of these values with the spectral values of authentic TPPO (272, 265, 259 and 223 nm) indicated that the reduced solution contained TPPO as a major species. Further evidence that one of the major products of the controlled-potential electrolysis of PPPI was TPPO was obtained by TLC followed by spectroscopic examinations. Through the spectroscopic examination of two major spots and comparison of authentic samples, it was ascertained that the spot with  $R_f$  value of 0.40 was TPPO and the other spot ( $R_f=0.82$ ) was TPP.

Because the latter spot appeared to be too large compared to the yield of TPP and TPPO obtained from quantitative analyses and to gain further insight into the spot, two-dimensional TLC technique was used. After the chromatograms were developed in one dimension with benzene-acetone the plates were removed from the developing chamber and were air-dried for several hours. The plates were then rotated through 90 degrees, immersed in the second solvent (dichloromethane), and developed. Thus *via* two-dimensional TLC experiments, we found that the high  $R_f$  value spot ( $R_f=0.82$ ) was

Table 4. Controlled-potential electrolysis results of triphenylphosphine phenylimide

Concn <sup>a</sup> , PPPI (mM)	Yield, moles product/moles starting material, %			
	TPP	TPPO	Diphenylphosphinic Acid	Aniline
1.67	10.7±1.1 <sup>b</sup>	26.5±2.0 <sup>b</sup>	34.4±0.5 <sup>b</sup>	70.9±0.9 <sup>b</sup>
2.26	14.7±0.6	23.7±1.9	32.3±2.0	74.7±5.3
3.50	15.8±0.7	18.6±1.4	26.1±1.4	77.3±1.1
4.76	12.5±0.5	18.1±1.0	32.3±5.2	82.6±5.8

<sup>a</sup> The acetonitrile solution contained 0.1 M TEAP and 10.9 mM water. Each concentration of the solution was run two or three times.

<sup>b</sup> Uncertainties are standard deviations from at least four measurements. These reflect only the precision of the final analytical step, not the precision of the over-all work-up.



resolved to two spots ( $R_f$  value of 0.03 and 0.77). The combined TLC and spectroscopic examinations of these two spots showed that they are TPPO ( $R_f=0.03$ ) and TPP ( $R_f=0.77$ ). Examinations of the authentic TPP by two-dimensional TLC experiments suggested TPP is not oxidized on the plate. Presumably, TPP and TPPO form a complex in the first solvent mixture.

The reduction of PPPI was carried out with consumption of 1e, 2e, 3e and 4e in order to ascertain the number of faradays required to consume all the starting material. The existence of the starting material in the incompletely reduced solutions, up to and including 3e reduction, was found by using TLC. These experiments also showed that TPP and TPPO were produced in every case.

In order to investigate additional products, the residue remaining after reduced pressure evaporation of the catholyte was examined. The white solid obtained by solvent (benzene) extractions of the residue was examined by TLC and it was found that the compound was resolved at  $R_f$  value of 0.15. A methanolic potassium hydroxide solution of the white solid was analyzed by UV absorption spectrophotometry; this solution exhibited four intense absorption peaks at 272, 265, 259 and 223 nm. In the absence of potassium hydroxide, the weak peak at 253 nm was not visible. Comparison of these values with the spectral values of phosphorus compounds reported by Jaffe, *et al.*<sup>22</sup> indicated that the methanol solution contained diphenylphosphinic acid. IR and NMR examinations of the compound further confirmed the presence of diphenylphosphinic acid. The spectra agreed well with the spectra of authentic material. The mass spectrum of this compound showed a base peak at  $m/e=217$  which corresponds to the primary fragment  $(C_6H_5)_2POO^+$

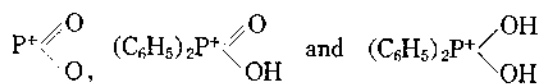
formed by loss of a proton from the molecular ion  $m/e=218$ ). Subsequent loss of water results in the fragment  $C_{12}H_8PO^+$  ( $m/e=199$ ). These combined spectroscopic results provide persuasive evidence for the formation of diphenylphosphinic acid in the electrolyzed solution.

The identification and quantitative analysis of aniline were carried out by gas chromatography. The gas chromatographic peak from the catholyte was trapped and the effluent was dissolved in cyclohexane and was analyzed by UV absorption spectrophotometry. This UV spectrum contained absorption maxima at 287 and 233 nm. They are the same as the absorption maxima for aniline.<sup>23</sup> Confirmation of aniline was obtained *via* another UV spectrum; the effluent was dissolved in 2.0 M hydrochloric acid and the UV spectrum of the acidic solution showed absorption maxima at 259, 253, 248 and 243 nm. These spectral values are well matched with those for authentic aniline hydrochloride.

The formation of benzene is established by gas chromatography and absorption spectrophotometric analysis of the electrolyzed solution; phenyl radicals formed by cleavage of preceding electrolysis products may abstract a hydrogen atom from the medium to form benzene. Previous workers<sup>5</sup> have reported that the phenyl radicals dimerize to form biphenyl when TPP is reduced in DMF. Results of analysis of electrolyzed solution by gas chromatography show that biphenyl is not present in our system at a detectable concentration. The limit of detection for biphenyl was found to be  $2.0 \times 10^{-3} \mu$  mole.

It was not possible to characterize completely the hygroscopic white crystalline solid which we isolated during the GC analysis for aniline. The following results, however, confirm that it is a derivative of  $(C_6H_5)_2PO_2^-$ . The physical properties of the unknown compound suggested a salt as a first guess, such as possibly an

ammonium perchlorate, but mass spectrum (MS) showed no substantiation for the presence of perchlorate. The mass spectrum of this compound showed very pronounced peaks at  $m/e=217$ , 218 and 219 with relative intensities very similar to those for authentic  $(C_6H_5)_2POOH$ . In addition, high resolution mass spectroscopic data gave excellent fits on these peaks for  $(C_6H_5)_2-$



(see Table 5). The UV spectrum was also very similar to  $(C_6H_5)_2POOH$  and the NMR spectrum showed the presence of phenyl group; however, both the UV and NMR spectra were distinctly different from those for  $(C_6H_5)_2POOH$ .

Thus, we conclude that the unknown compound is a derivative of  $(C_6H_5)_2PO_2^-$ ; it could be a salt of the anion or an ester. The material was dissolved in 1.0 M potassium hydroxide solution and was then extracted with ether. If the material is a salt, presumably the anion  $(C_6H_5)_2PO_2^-$  would stay in aqueous phase and free base would be extracted into ether. Both phases, however, showed identical UV spectra, a result which suggests the ester postulate may be correct. In order to characterize the remain-

der of the molecule we obtain a 20 eV MS; however, the greatest  $m/e$  of any prominence were still 217~219. Since a molecular ion does not appear, we compared the MS of the unknown with that of authentic  $(C_6H_5)_2POOH$  and then picked out some of the prominent peaks which are not present in MS of authentic sample. It was hoped that these fragments would give a clue to the structure of rest of the molecule (see Table 5). Although here is not enough information for a definite structure determination, there is some indication from the composition of these fragment ions that the rest of the molecule does contain nitrogen. In addition the IR spectrum showed a broad absorption in the region of 2.93~3.02  $\mu$ .

Assuming aniline and the unknown compound have approximately equal GC response on an area and mole basis, the incompletely characterized material appears to be present in sufficient quantity to account for the phosphorus not found in other products. Assuming that the UV spectrum of the unknown compound is due entirely to  $(C_6H_5)_2PO_2^-$  and the molar absorptivity of the absorption peak at 264 nm is the same both the unknown compound and  $(C_6H_5)_2POOH$ , the incompletely characterized material

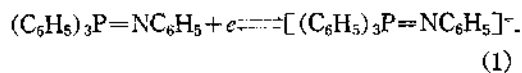
Table 5. Summary of physical and spectral data for the incompletely characterized compound.

1. physical Properties	Very hygroscopic, white crystalline solid. Soluble in water, acetonitrile and acetone. Insoluble in benzene, chloroform and carbon tetrachloride. Melting point 75°
2. Spot test	Positive for phosphorus by ammonium molybdate—benzidine.
3. TLC	$R_f=0.03$ on the silica gel GF-254, solvent mixture is benzene/acetone (75/25).
4. GC	5.0 % diethylene glycole column at 125° with a retention time of 7.2 minutes.
5. NMR(acetone- $d_6$ ) (vs. TMS)	1.89 (s) Integration gives a 13 : 10 ratio for singlet (s) and multi- 6.41~6.80 (m) plet (m) peaks.
6. UV (MeCN) (nm)	238, 289
7. IR (KBr)	2.93~3.02
(a)	6.10~6.14
	7.25
	8.92

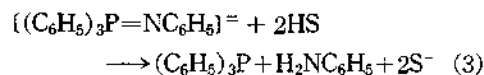
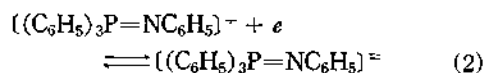
accounts for 22.5% of the total phosphorus on the basis of a simple calculation of 4.76 mM PPPI. The molar absorptivity used was 1170 which was calculated from a standard solution containing authentic  $(C_6H_5)_2 POOH$  in acetonitrile. The absorbance of the unknown at 264 nm in ether solution was 0.78 and in aqueous solution was 0.74. The total volume of both solutions was approximately 40 ml. A summary of the physical and spectral data for the compound is given in Table 5.

The results described here show that the overall reduction indicates an  $n$  apparent of 4 during coulometric reduction, and that the primary electrode process is followed by chemical reactions which produce products electroactive at the working cathode potential. In addition to this, the qualitative picture obtained from cyclic voltammetry showed total lack of anodic current corresponding to the reoxidation of the reduced products and the current function decreases as the scan rate increased (Case VI in the work of Nicholson and Shain<sup>21</sup>), all of which are consistent with an ece-type mechanism<sup>20</sup>. The quantitative results for controlled-potential electrolysis are presented in Table 4. In addition to these, the products included benzene and an incompletely characterized compound.

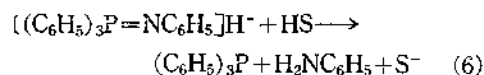
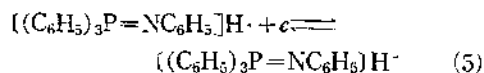
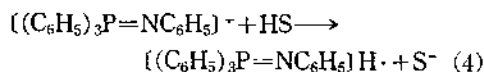
Clearly, the mechanism of the reduction of PPPI in acetonitrile is more complicated than that of simple organic compounds (e. g., aromatic hydrocarbons, azocompounds<sup>24</sup>). The voltammetric and controlled-potential electrolysis results suggest a reduction mechanism possibly of the following type. For the first step in the reduction of PPPI a mechanism in which a one-electron transfer leads to the formation of anion radical can be suggested.



It is also evident that the anion radical is consumed by some fairly fast reaction since no reverse current was obtained in cyclic voltammetry. The experimental results are best explained by assuming that the anion radical formed can immediately add a second electron at the applied potential to form PPPI dianion. Further, the dianion may react with a protonating agent (HS) present in the medium, such as traces of water, the solvent itself, etc.



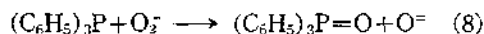
Another possible reduction pathway could be postulated by assuming that the anion radical may undergo chemical reaction with a protonating agent. The following reduction mechanism can be suggested:



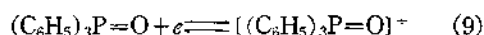
The formation of TPP and aniline indicate that the reaction occurs by cleavage of the phosphorus—nitrogen double bond, while the nitrogen—phenyl linkage remain intact. The known reduction potential of TPP shows that it is not reduced at the cathode potential and no reduction of aniline is observed in the 0 to -2.8 V vs. sce potential range.

The triphenylphosphine oxide isolated from the electrolyzed solution may be formed by a reaction of TPP with the peroxide anion<sup>25</sup> formed by the reaction of oxygen.

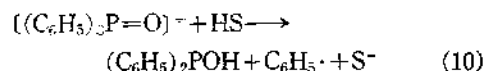




Little is known concerning above reactions beyond the fact the product indicated has been detected. The voltammetric data support the view that TPPO proceeds by a one electron reduction of the anion radical<sup>5,27</sup>.



Controlled-potential coulometry and product analysis suggest that the reaction of TPPO anion radical is as follows.



Diphenylphosphinic acid is probably formed during the work-up of the electrolyzed solution. Diphenylphosphinous acid is known to be unstable and presumably reacts with oxygen to produce diphenylphosphinic acid.

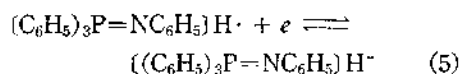
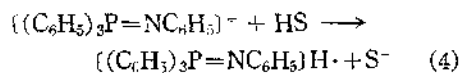
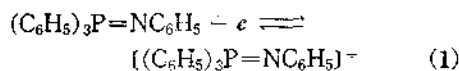
A similar cleavage of a phenyl group from the phosphorus-phenyl linkage to phenyl radical and diphenylphosphide anion has been proposed by Santhanam and Bard<sup>5</sup> in the reduction of TPP. Analogous phenyl cleavage of TPPO by sodium was reported by Hoffman and Tesch<sup>29</sup>. This is an excellent example of the direct comparison of electrochemical and chemical reactions. They suggested that after the initial formation of a radical anion—either absorbed at the metal surface or in low concentration in solution—it collapses to phenyl radical and phosphide or phosphinite anion. The predominant portion of the cleaved phenyl group forms benzene. Thus the formation of diphenylphosphinic acid and benzene is in agreement with the products obtained by the reaction of sodium with TPPO in 1,2-dimethoxyethane(DME).

Cowley and Hnoosh<sup>3</sup> also suggested that the nature of free radical species derived from TPPO depends on the alkali metal and the solvent. Reduction of TPPO with potassium in tetra-

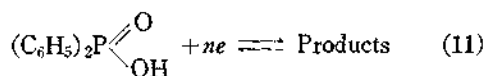
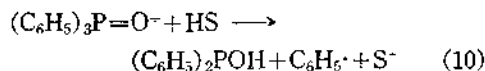
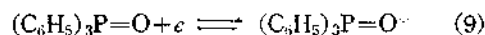
hydrofuran(THF) at  $-10^\circ$  resulted in a blue solution with a 2S-line epr spectrum. By contrast, potassium reduction in DME resulted in a red-brown solution with a 10-line spectrum. They reported that the species in THF solution is TPPO and the 10-line spectrum has a very similar appearance to that reported for  $(\text{C}_6\text{H}_5)_2\text{P}^-$  by Britt and Kaiser.<sup>30</sup>

The difficulty in observing an epr spectrum of TPPO anion radical<sup>3,28</sup> and our results indicate that the TPPO anion radical is unstable. It seems reasonable that previous nonaqueous electrochemical studies on organo-phosphorus system<sup>3,5</sup> show that if the phosphorus atom is actively involved in the electroactive group, the product is generally unstable and decomposes rapidly.

Since the current function of the cathodic wave of PPPI decreases with increasing sweep rates in cyclic voltammetric data, it seems likely that a chemical reaction is closely coupled to the primary electroreduction.



An additional ece type process involving TPPO can be postulated to account for the observation of  $(n > 2)$



We conclude that the reduction of PPPI can be characterized as both the ec and ece mechanisms, where an ec mechanism involves reac-

tion of the electrogenerated product to a non-electroactive species, while an ece mechanism implies the product of the chemical reaction is reduced at the potential where PPPI is reduced.

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