Solutions of 100 μl of benzene-1,3,5-d_3 in 20 ml of hexadecane were irradiated at room temperature for periods of 5 and 17.5 hr after first flushing with nitrogen. The absorbance of the solutions at 2537 Å increased by 30% in the former case and by 100% in the latter. Reported values for the quanta absorbed per molecule of benzene were corrected for this effect. The irradiated benzene was recovered from the hexadecane solution by evacuation, ultimately at 50° and 10^{-4} mm. More than 90% of the initial benzene was recovered.

Similar irradiation procedures were employed to measure the rates of related reactions. The amount of benzvalene present after a 15-min irradiation of a solution of 100 μl of benzene in 20 ml of hexadecane was determined by gas chromatographic analysis[4] of the recovered benzene. The formation of methoxybicyclohexenes[4,7] in a 4-hr irradiation of 100 μl of benzene in 20 ml of acidified methanol (0.2% HCl) and of 1,3-cycloaddition products[8] in a 30-min irradiation of 100 μl of benzene in 20 ml of cyclopentene was also determined.

Vapor Phase, 2537 Å. A dewar-type cell was used to provide a large surface and thus minimize absorption by deposited polymer. The vessel had an inner wall of 43-mm o.d. Vycor 7910, an outer wall of 69-mm o.d. quartz, a path length of 1.1 cm, and a volume of 400 ml. A coiled low-pressure mercury lamp (Nester and Faust NFUV-300) within the well delivered 3.8×10^{21} quanta/hr of 2537-Å radiation to a solution of uranyl oxalate in the cell. Weighed benzene samples in vacuum-sealed fragile tubes were introduced into the cell before evacuation and seal-off. The absorption of light by the benzene was calculated using a measured molar extinction coefficient of 120. Transmission through the cell was observed to decrease during the irradiations. In view of the temperature gradient (*ca.* 20°) across the cell, it was assumed that most of the polymer deposition occurred on the outer wall, and that the intensity of the light available to benzene did not decrease. This assumption is supported by the correspondence of quantum yields in runs V-1 and V-2 in which exposures differed by a factor of 5. If the assumption is not correct, quantum yields may be somewhat greater than those reported. Recoveries of benzene were 95% in runs V-1 and V-3 and 80% in run V-2.

Vapor Phase, 2480 Å. A cylindrical quartz cell with a diameter of 43 mm, a volume of 145 ml, and a 10-cm light path was used. The light source was a Bausch and Lomb SP-200 super-pressure mercury lamp and high-intensity grating monochromator, set at 2480 Å. Although the slit widths permitted a band pass of 96 Å, almost all of the light was absorbed between 2465 and 2490 Å. The output of the lamp, *ca.* 1.5×10^{19} quanta/hr, was measured with a potassium ferrioxalate actinometer. Absorption by benzene was determined by measuring the light transmitted through the (evacuated) cell before and after the sealed sample tube was opened. During irradiation the cell was rotated continuously, and reversed once, in order to distribute the light, and the deposited polymer, over as large a surface as possible. Periodically, the cell was removed and the intensity of the incident light was remeasured. At these times, the benzene was condensed in a side arm, and the transmission of the cell at 2480 Å was measured in a Cary spectrophotometer.

(In run V-5 the lamp output decreased by 24% and the optical density of the cell increased by 0.21 during the 30-hr irradiation.) It was assumed, on the basis of visual examination, that the decreased transmission resulted from deposits on the incident window. Absorption of light by benzene in each interval was calculated from the average light intensity and the average transmission of the incident window. Recovery of benzene was 96% in run V-4 and 93% in run V-5.

Nitration. The procedure was adapted from that of Melander.[10] The recovered benzene was distilled *in vacuo* onto ten times its volume of nitrating mixture (1:2 HNO_3:H_2SO_4). The reaction tube was sealed off, warmed to room temperature, and shaken for 10 min. The contents were transferred to crushed ice and the crude dinitrobenzene was washed with water. All but the smallest sample were recrystallized twice from 75% ethanol. Those samples in which the extent of rearrangement was small were subjected to gas chromatography (Carbowax 20M, 155°) to further decrease the content of *o*-dinitrobenzene. The smallest sample (run V-5) was purified only by gas chromatography.

Samples of unirradiated benzene-1,3,5-d_3 were nitrated similarly, and the products were purified by each of the three procedures.

Mass Spectrometry. The purified samples of dinitrobenzene were analyzed on a 12-in. sector mass spectrometer with an ionizing potential of 70 v. The solid samples were introduced with a probe into the heated (150°) gas inlet system. The parent mass region was scanned repeatedly in both directions; reported intensities are averages of twelve scans. Mole fractions of the various deuterated dinitrobenzenes were calculated from the ratio of their parent peaks, corrected for ^{13}C, ^{15}N, and ^{18}O contributions from molecules of lower deuterium content, to the sum of all the corrected parent peaks. The mole fraction of rearranged trideuteriobenzene was assumed to be 1.5 times the increase in mole fraction of dideuteriodinitrobenzene in an irradiated sample over that in the blank.

Acknowledgments. We are grateful to Professor W. A. Noyes, Jr., for many helpful discussions and suggestions. We also thank Dr. C. A. Parker and Professor F. Wilkinson for helpful comments.

Electrochemistry of Organophosphorus Compounds. II. Electroreduction of Triphenylphosphine and Triphenylphosphine Oxide

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Abstract. The electrochemical reduction of triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO) has been investigated using polarography, cyclic voltammetry, coulometry, and product analysis. The reduction of TPP proceeds by a one-electron transfer to form the anion radical which undergoes cleavage of a phenyl group.

Several recent papers have been concerned with the polarography of triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO)[2,3] and the electron spin resonance (esr) spectroscopic investigation of radicals derived from alkali metal reduction of these. Hanna[4] claimed, partly on the basis of polarographic evidence of a one-electron reversible reduction,[2] that he

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[1] To whom correspondence and request for reprints should be directed.

[2] S. Wawzonek and J. H. Wagenknecht, "Polarography—1964," Macmillan and Co., Ltd., London, 1966, p 1035.

[3] R. E. Dessy, T. Chivers, and W. Kitching, *J. Am. Chem. Soc.*, **88**, 467 (1966).

[4] M. W. Hanna, *J. Chem. Phys.*, 37, 685 (1962).

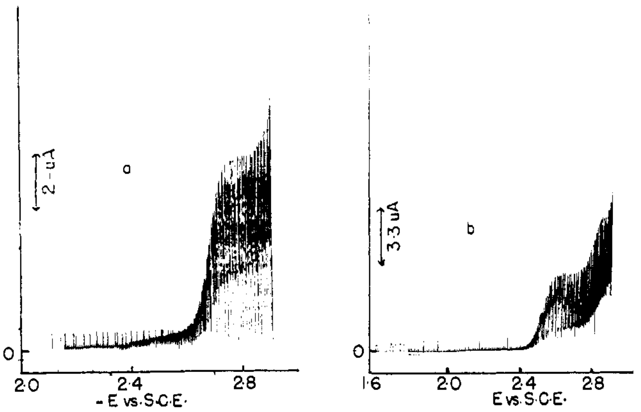

Figure 1. (a) Polarogram for the reduction of triphenylphosphine. The solution contained 0.1 *M* TBAI and 2.38 m*M* TPP in DMF. (b) Polarogram for the reduction of triphenylphosphine oxide. The solution contained 0.1 *M* TBAI and 1.32 m*M* TPPO in DMF.

obtained triphenylphosphine anion radical. Other investigators, however, found only biphenyl anion radical[5] or diphenylphosphine radical[6] produced under similar conditions. The present investigation was undertaken to study the mechanism of the electroreduction of TPP and TPPO by a variety of electrochemical methods, with special reference to the stability of the anion radicals. The first paper in this series[7] showed that tris-(*p*-nitrophenyl)phosphate undergoes a cleavage reaction following the initial reduction step.

Results

Voltammetric Methods. Triphenylphosphine. Polarographic reduction of triphenylphosphine (TPP) at a dropping mercury electrode in N,N-dimethylformamide (DMF) containing 0.1 *M* tetra-*n*-butylammonium iodide (TBAI) showed one wave with a half-wave potential of −2.70 V *vs.* an aqueous saturated calomel electrode (sce) (Figure 1a). Tomes criterion for reversibility, $E_{3/4} - E_{1/4}$, was 62 mV, suggesting a reversible or quasi-reversible one-electron transfer. The wave height of this wave varied as the square root of the head of the dme ($h^{1/2}$), indicating a diffusion-controlled process. At 3° the half-wave potential was −2.69 V *vs.* sce and $E_{3/4} - E_{1/4}$ was 56 mV. Based on the polarographic results and assuming $n = 1$, the diffusion coefficient of TPP is calculated to be 0.54×10^{-5} cm²/sec at 25° and 0.24×10^{-5} cm²/sec at 3°.[8]

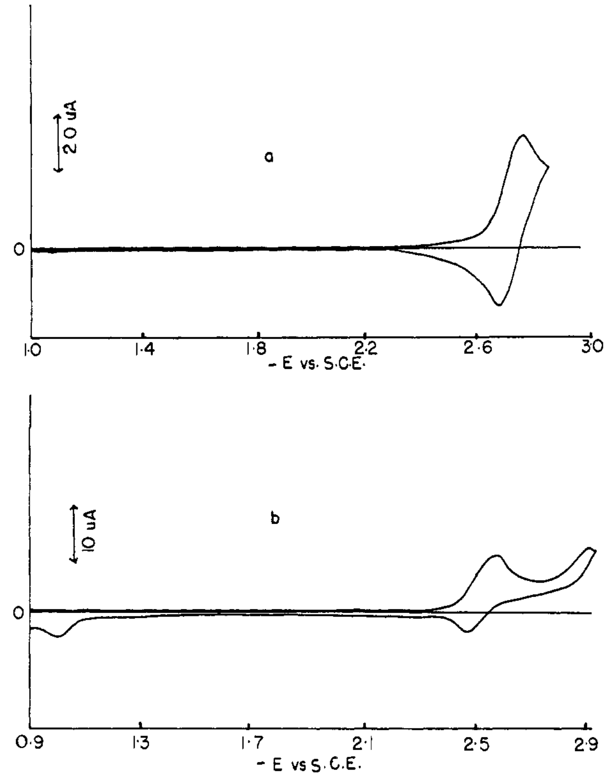

Figure 2. Cyclic voltammetric curves for (a) TPP and (b) TPPO in 0.1 *M* TBAI in DMF.

A solution of TPP in DMF containing 0.1 *M* TBAI when examined by cyclic voltammetry at a hanging mercury drop electrode (hmde) showed a reduction peak at −2.75 V *vs.* sce and on reversal of scan an oxidation peak at −2.68 V (Figure 2a). The results of cyclic voltammetric experiments are given in Table I.

Table I. Cyclic Voltammetric Data for Reduction of Triphenylphosphine

Sweep rate, mV/sec	i_{pc}, μA	i_{pa},[a] μA	i_{pa}/i_{pc}[b]	E_{pc}, V *vs.* sce	E_{pa}, V *vs.* sce
		Without Proton Donor			
67.1	5.3	5.0	0.90	−2.75	−2.68[c]
153	7.8	9.0	0.97	−2.75	−2.68[c]
222	9.1	11.0	1.01	−2.75	−2.68[c]
312	11.2	12.9	0.99	−2.75	−2.68[c]
476	13.4	15.7	1.00	−2.76	−2.68[c]
712	15.6	18.4	1.06	−2.76	−2.66[c]
222	20.0	20.0	1.00	−2.75	−2.68[d]
		With Proton Donor			
222	86.0	...	...	−2.76	...[e]
222	142.0	...	...	−2.82	...[f]

[a] Estimated by using extrapolation of cathodic current as base line. [b] Calculated using Nicholson's semiempirical method[10] to obtain i_{pa}. [c] The solution contained 0.1 *M* TBAI and 0.59 m*M* TPP in DMF. The working electrode was hmde. Auxiliary electrode was silver wire. Potentials *vs.* sce, may include some uncompensated *iR* drop. [d] The concentration of TPP was 2.28 m*M*. [e] The solution contained 2.28 m*M* TPP and 0.014 *M* hydroquinone. [f] This solution contained 2.28 m*M* TPP and 0.03 *M* hydroquinone.

The ratio of i_{pa}/i_{pc}, where i_{pa} and i_{pc} are the anodic and cathodic peak currents, respectively, calculated using the semiempirical method suggested by Nicholson[10]

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(5) (a) A. K. Hoffman and A. G. Tesch, *J. Am. Chem. Soc.*, **81**, 5519 (1959); (b) D. Chapman, S. H. Glarum, and A. G. Massey, *J. Chem. Soc.*, 3140 (1963).

(6) (a) A. D. Britt and E. T. Kaiser, *J. Phys. Chem.*, **69**, 2775 (1965); (b) A. H. Cowley and M. H. Hnoosh, *J. Am. Chem. Soc.*, **88**, 2595 (1966).

(7) K. S. V. Santhanam, L. O. Wheeler, and A. J. Bard, *ibid.*, **89**, 3386 (1967).

(8) This value differs significantly from that calculated from the I_d value given by Wawzonek and Wagenknecht,[2] 0.18×10^{-5} cm²/sec (25°) under similar conditions. However, in the calculation of this I_d value, the dme values of *m* and *t* used were those obtained at open circuit in distilled water (J. H. Wagenknecht, private communication, May 1967). Since the interfacial tension, σ, between mercury and the solution is smaller for DMF than for water (*e.g.*, at the electrocapillary maximum, $\sigma_{H_2O} = 470$ dynes/cm and $\sigma_{DMF} = 376$ dynes/cm[9]), the *mt*, which is proportional to σ, will be smaller in DMF. Moreover, *t* is much smaller at the very negative potentials of the polarographic wave of TPP as compared with the open-circuit value. We conclude that the apparent I_d value reported in ref 1 is smaller than the actual one calculated with *m* and *t* values extant at the conditions at which I_d is measured. Our value for the diffusion coefficient of TPPO similarly differs from that given in ref 2.

(9) V. D. Bezuglyi and L. A. Korshikov, *Soviet Electrochem.*, **1**, 1279 (1965).

(10) R. S. Nicholson, *Anal. Chem*, **38**, 1406 (1966)

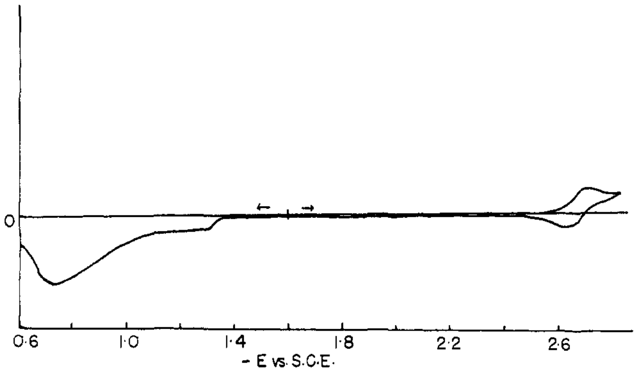

Figure 3. Cyclic voltammetric curve of TPP after controlled-potential reduction at −2.80 V *vs.* sce.

Table II. Cyclic Voltammetric Data for the Reduction of Triphenylphosphine Oxide[a]

Sweep rate, mV/sec	First peak					Second peak	
	i_{pc}, μA	i_{pa},[b] μA	i_{pa}/i_{pc}[c]	E_{pc}, V	E_{pa}, V	i_{pc}, μA	E_{pc}, V
67.1	23.6	22.4	0.94	−2.60	−2.52	30.0	−2.88
153	33.6	35.0	1.04	−2.60	−2.52	41.2	−2.92
222	40.6	44.8	1.10	−2.60	−2.52	47.6	−2.94
312	48.0	51.8	1.08	−2.60	−2.52		
476	56.2	60.0	1.06	−2.60	−2.52		
714	65.0	70.0	1.08	−2.60	−2.52		

[a] The solution contained 0.1 *M* TBAI and 3.14 m*M* triphenylphosphine oxide in DMF; other data as in Table I. [b] Estimated by using extrapolation of cathodic current as base line. [c] Calculated using Nicholson's semiempirical method[10] to obtain i_{pa}.

is constant and near one. The current function (proportional to $i_p/v^{1/2}$) for this reduction is also constant with scan rate. These results indicate that the reduction product is stable during the time of the sweep.

The results obtained in acetonitrile differ significantly from those in DMF. In acetonitrile containing 0.1 *M* TBAI the cyclic voltammetric peak occurs at −1.60 V *vs.* sce and appears irreversible. Since there was a wide difference in potentials for the reduction in DMF and acetonitrile, we suspected a chemical reaction between TPP and acetonitrile. A spectrophotometric examination of a solution of TPP in acetonitrile showed absorption spectra with maxima at 270, 260, and 252 mμ, while in DMF, only an absorption maximum at 260 mμ, which is also reported for TPP in ethyl alcohol, is observed.[11] This suggests that the observed reduction process is not that of TPP, but a product of a TPP–acetonitrile reaction. For example, it has been reported[12] that TPP reacts with halogenated acetonitriles to form cyanomethylene triphenylphosphorane.

The effect of a proton donor on the reduction of TPP was studied by adding hydroquinone to the DMF solutions containing 0.1 *M* tetra-*n*-butylammonium iodide and TPP. Results are shown in Table I. The reduction peak shifts to more negative potentials and broadens with an increase in the height of the peak and the voltammetric wave becomes irreversible. The peak potential shifts in a negative direction with increasing scan rates, a characteristic of irreversible waves.[13] The number of electrons involved in the reduction is calculated from peak currents to be about 4, when a sufficient excess of proton donor is present.

Triphenylphosphine Oxide. Electrochemical reduction of triphenylphosphine oxide (TPPO) is quite different from that of triphenylphosphine. Polarographic reduction of a solution of TPPO in DMF containing 0.1 *M* TBAI gives two reduction waves with $E_{1/2}$ values of −2.51 and −2.84 V *vs.* sce (Figure 1b). The wave height of both waves varied with $h^{1/2}$. The difference, $E_{3/4} - E_{1/4}$, was 60 mV for the first wave and 62 mV for the second. The diffusion coefficient for the TPPO calculated with the Ilkovic equation, assuming $n = 1$, is 2.35×10^{-5} cm^2/sec.

The cyclic voltammetry at a hmde in DMF showed two reduction peaks at −2.54 and −2.87 V *vs.* sce (Figure 2b). Results are given in Table II. The current function and the ratio i_{pa}/i_{pc} are constant with scan rate. The current function for the second reduction decreases with increasing scan rate and the peak potential of the second reduction shifts with increasing scan rate. This reduction is followed up by a chemical reaction which yields a species oxidizable at about −1.0 V *vs.* sce (see Figure 2b). This oxidation wave is not observed when the potential scan is reversed at potentials less negative than the second reduction peak.

The polarographic reduction of TPPO in dimethyl sulfoxide (DMSO) differs from that in DMF. Only one drawnout wave with $E_{1/2}$ at −2.41 V *vs.* sce and $E_{3/4} - E_{1/4}$ of 140 mV was observed. The *n* value calculated from the diffusion current is about 3, when the diffusion coefficient found in DMF, corrected for differences in the viscosity (η) of the two solvents (η_{DMF} = 0.80 cps and η_{DMS} = 1.96 cps),[14] is used.

Cyclic voltammetry in DMSO containing TBAI also showed results different from that obtained in DMF. At slow scan rates (less than 153 mV/sec) two peaks at −2.44 and −2.51 V *vs.* sce are observed. The first peak merges with the second at faster sweeps (>222 mV/sec) to give a single broad peak. No anodic peaks are observed on reversal at any scan rate. These results suggest a reaction between TPPO or its reduction products and DMSO.

Controlled-Potential Coulometry. Triphenylphosphine. The reduction at a mercury pool electrode on the plateau of the wave (−2.80 V *vs.* sce) was undertaken to examine the nature of reduction products. Since the potential for reduction is close to the background discharge potential (−2.95 V *vs.* sce), conditions for controlled-potential coulometry are not favorable. The area of the mercury pool electrode was about 10 cm^2 and a solution volume of 25 ml was employed. The current during the reduction, initially 35.2 mA in one of the experiments (concentration 1.5 m*M*), decayed down to a steady-state value of 13.9 mA. The electrolysis was stopped at this steady-state current, and the orange-yellow solution was examined by cyclic voltammetry, ultraviolet absorption spectrophotometry, and chromatography. The cyclic voltammogram of the orange-yellow solution is shown in Figure 3. With the sweep started at −1.50 V on a cathodic scan, a peak at −2.71 V with a reversal peak at −2.66 V appeared. When the scan was initially anodic, stirring of the hmde occurs, and two anodic peaks, at −1.32 and −0.72 V,

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(11) H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, 74, 1069 (1952).

(12) G. P. Schiemenz and H. Engelhard, *Chem. Ber.*, **94**, 578 (1961).

(13) R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).

(14) I. M. Kolthoff and T. B. Reddy, *J. Electrochem. Soc.*, **108**, 980 (1961).

Table III. Cyclic Voltammetric Data before and after Controlled-Potential Reduction[a]

Conditions	Initial reduction				Initial oxidation			
	E_{pc}, V	i_{pc}, μA	E_{pa}, V	i_{pa}, μA	E_{pa}, V	i_{pa}, μA	E_{pa}, V	i_{pa}, μA
Before electrolysis (TPP)	−2.75	15.0	−2.67	15.0	...	...	...	...
Reduced solution	−2.71	6.2	−2.66	6.2	−1.32	6.2	−0.72	57.0
Biphenyl	−2.71	...	−2.66	...	...	...	...	...

[a] Sweep rate, 153 mV/sec.

were observed. Values of reduction and oxidation currents obtained before and after controlled-potential electrolysis are given in Table III. To determine the identity of the new systems, a comparison of peak potentials with those of various known compounds was made. The reduction peak at −2.71 V *vs.* sce agreed well with a biphenyl system. Using the diffusion coefficient reported[15] for biphenyl, 1.20×10^{-5} cm^2/sec, and the peak currents before and after controlled-potential electrolysis, the concentration of biphenyl is calculated to be about half of the original concentration of TPP.

The orange-yellow product was investigated further using uv spectroscopy, gas chromatography, and thin layer chromatography. The product solution was extracted with hexane, which was then evaporated under reduced pressure. The resulting solid was dissolved in 95% ethanol; this solution showed ultraviolet absorption maxima at 225, 260, 265, and 272 mμ. Comparison of these values with the spectral values of the phosphorus compounds reported by Jaffé, *et al.*,[11] indicated that the ethanol solution contained diphenylphosphinic acid. A biphenyl spectrum, with a maximum at 247 mμ, was not visible because its concentration was smaller and its extinction coefficient is about the same as diphenylphosphinic acid. However, when the residue was extracted with ether, only the biphenyl absorption maximum was present. The absence of TPP with its maxima at 202 and 263 mμ indicated the catalytic behavior observed in coulometry was not due to simple reoxidation of the reduction product of TPP. This is supported further by the absence of a spot in thin layer chromatography for TPP (R_f = 0.69) and the appearance of a new spot with R_f = 0.55. This new spot agreed well with the R_f value of biphenyl. Additional evidence for biphenyl was obtained by gas chromatography. Three peaks corresponding to air, the solvent, and biphenyl were obtained when the product solution was analyzed.

Triphenylphosphine Oxide. Controlled-potential reductions of TPPO were carried out in DMF containing either TBAI or bromide as supporting electrolytes at a large mercury pool electrode with its potential controlled at −2.6 V *vs.* sce. Again the final value of the steady-state current was much higher than the background value, suggesting a chemical reaction following the charge transfer, in which an electroactive species is constantly regenerated. When the electrolyzed solution was examined by cyclic voltammetry, there were two initial oxidation peaks at −1.00 and −0.76 V *vs.* sce and two initial reduction peaks at the same potentials as those of TPPO. The electrolyzed solution, when examined by ultraviolet absorption spectrophotometry, gave only a peak identifiable as TPPO, at 264 mμ.

Discussion

The mechanism of the reduction of triphenylphosphine in DMF, as observed is polarography and cyclic voltammetry, appears to proceed by a transfer of an electron to form an anion radical

$$(C_6H_5)_3P + e \longrightarrow (C_6H_5)_3P^- \qquad (1)$$

When an *intra muros* esr generation was attempted at 3°, a weak signal, indicating an unstable radical, was obtained. Controlled-potential coulometry and analysis of products suggests that the reaction of TPP anion radical is as follows.

$$(C_6H_5)_3P^- \xrightarrow{SH} (C_6H_5)_2PH + C_6H_5\cdot + S^- \qquad (2)$$

$$2C_6H_5\cdot \longrightarrow C_6H_5\text{–}C_6H_5 \qquad (3)$$

$$C_6H_5\text{–}C_6H_5 + e \longrightarrow C_6H_5\text{–}C_6H_5\cdot^- \qquad (4)$$

Diphenylphosphinic acid is probably formed during the workup of the electrolyzed solution. Diphenylphosphineis known to react with oxygen to produce diphenylphosphinic acid. The occurrence of biphenyl is established by product analysis and electrochemical behavior; biphenyl is known to show catalytic behavior during its coulometric reduction in DMF. This cleavage to form biphenyl agrees with previous workers[5] who found only the esr spectrum of biphenyl anion radical when TPP was reduced with alkali metal in dimethoxyethane. Britt and Kaiser[6a] also report the occurrence of biphenyl during the alkali metal reduction of TPP, although only in small amounts. Our results indicate that the TPP anion radical is unstable in DMF over time periods greater than those involved in polarographic and cyclic voltammetric experiments and that polarographic evidence of a one-electron reaction is not sufficient for postulating the existence of a radical stable enough for esr spectroscopic examination.

It has been reported[2] that TPP and TBAI react in DMF to form triphenyl-*n*-butylphosphonium iodide. We have found no evidence for this reaction at room temperature during our experiments. Since triphenyl-*n*-butylphosphonium iodide is reduced at −1.87 V, it would clearly be visible in cyclic voltammetric experiments. We did not obtain TPPO as a product, even during electrolysis in the presence of air.

The effect of addition of proton donor (*e.g.*, hydroquinone) appears complicated. Since the potential shifts toward more negative values with increasing amounts of donor, a preprotonation reaction is suggested, *e.g.*

$$(C_6H_5)_3P + H^+ \rightleftharpoons (C_6H_5)_3PH^- \qquad (5)$$

The over-all reduction indicates $n \sim 4$ during voltammetry and a catalytic reaction during coulometric reduction, and probably involves chemical reactions producing products electroactive at the potentials of the wave (an ece-type mechanism).

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(15) T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, *J. Am. Chem. Soc.*, 87, 121 (1965).

The reduction of TPPO on the polarographic and voltammetric time scale probably proceeds by a one-electron reduction to the anion radical

$$(C_6H_5)_3PO + e \rightleftarrows (C_6H_5)_3PO\cdot^- \qquad (6)$$

The second wave represents further reduction probably followed by a fast chemical reaction. During large-scale electrolysis, a catalytic reaction is observed, and, since TPPO is recovered from the electrolyzed solution, this reaction probably involves a reaction of the anion radical to regenerate TPPO. The oxidation peaks found after coulometric reduction are probably caused by products of an undefined side reaction.

Experimental Section

The general experimental methods and purification techniques are the same as those previously described.[16] A multipurpose instrument employing operational amplifier circuitry with three-electrode configuration was used in voltammetric experiments. The reference electrode was an aqueous sce connected *via* an agar plug and sintered glass disk. All potentials quoted are with reference to this electrode.

Triphenylphosphine was obtained from Carlisle Chemical Works and triphenylphosphine oxide from Aldrich Chemical Co. TPP was recrystallized from diethyl ether to yield white plates with a melting point of 81°. The TPPO used had a melting point of 159°. The purity was further tested by thin layer chromatography. The TBAI was polarographic grade, obtained from Southwestern Analytical Chemicals (Austin, Texas).

The thin layer chromatography experiments were carried out on Eastman chromoplate activated at 100° for 30 min. The eluent was 70% pentane–methylene chloride. Iodine was used for developing the chromatogram.

A Chrom Alyser 100 (Dynatomic Instruments) was used for gas-liquid chromatography. The column used for identification purposes was 5% SE 30 on Chromosorb W, 30–60 mesh ($^1/_8$ in. × 6 ft) at 240°.

Acknowledgment. This work was performed under Contract DA-18-035-AMC-715(A), U. S. Army Edgewood Arsenal. The help of L. O. Wheeler in esr experiments is gratefully acknowledged.

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Reactions of He^3H^+ Ions with Gaseous Hydrocarbons. II. Methane and Ethane

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Abstract: The reactions of the He^3H^+ molecular ion, formed from the decay of gaseous tritium, with methane and ethane at atmospheric pressure were investigated under conditions ensuring that the labeled decay ions were the only source of the tritiated products, with no interference from radiolytic processes. The He^3H^+ exothermically protonate the methane, giving excited $CH_4{}^3H^+$ ions, that can be either collision stabilized at 760 torr or decompose into tritiated methyl ions and hydrogen. The stabilized ions react with CH_4 according to a thermoneutral proton-transfer process, which yields the observed tritiated methane, while the methyl ions react with CH_4 forming the highly unreactive ethyl ions, whose fate depends on the nature and the amount of the impurities contained in the system. The reaction of the He^3H^+ ions with ethane yields excited $C_2H_6{}^3H^+$ ions, which appear to decompose into labeled ethyl ions, without any appreciable stabilization. The thermoneutral hydride ion transfer from the C_2H_6 to the labeled ethyl ions leads to the formation of the observed tritiated ethane.

In recent years, a considerable amount of work was devoted to the study of the reactions of protonating agents, such as CH_5^+,[1–3] H_3^+ and D_3^+,[4,5] CHO^+, etc.,[6–9] with a variety of gaseous hydrocarbons. All such investigations were carried out with mass spectrometric techniques, at pressures ranging from 10^{-4} to 2 torr.

In the first paper of this series,[10] it was shown that, under suitable experimental conditions, the β decay of molecular tritium affords a convenient means of producing a very reactive protonating reagent, the He^3H^+ ion, within gaseous systems at any pressure, and of identifying, by tracer techniques, the labeled products formed from its interactions with the organic substrate.

The present paper describes the application of such a technique to the study of the reactions of the He^3H^+ ions in the simpler alkanes, methane and ethane.

Experimental Section

Materials. The tritium gas, obtained from CEA (France), with a stated purity of 95%, was subjected to a careful radio gas chromatographic analysis, in order to establish the nature and the amount of any radioactive impurity.

The content of hydrogen tritide was measured using an 8-m silica gel column, cooled to liquid nitrogen temperature.[11] The outlet of the column was connected to a 25-ml flow ionization chamber, whose current was measured with an electrometer (Model

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