Electrochemistry of organophosphorus compounds. II. Electroreduction of triphenylphosphine and triphenylphosphine oxide

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Solutions of 100 μl of benzene-1,3,5-d3 in 20 ml of hexadecane were irradiated at room temperature for periods of 3 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 analysis1 of the recovered benzene. The formation of methoxybicyclohexenes1,2 in a 4-hr irradiation of 100 μl of benzene in 20 ml of acidified methanol (0.2% HCl) and of 1,3-cycloaddition products8 in a 30-min irradiation of 100 μl of benzene in 20 ml of cyclohexene was also determined.

Vapor Phase, 2537 Å. A dewar-type cell was used to provide a large surface and to 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 cooled low-pressure mercury lamp (Nester and Faust NFUV-300) within the well delivered 3.8 × 1011 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 did not decrease. We also thank Dr. C. H. Wawzonek and Allen J. Bard

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

K. S. V. Santhanam and Allen J. Bard

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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)3, and the electron spin resonance (esr) spectroscopic investigation of radicals derived from alkali metal reduction of these. Hanna4 claimed, partly on the basis of polarographic evidence of a one-electron reversible reduction,3 that he...
obtained triphenylphosphine anion radical. Other investigators, however, found only biphenyl anion radical or diphenylphosphine radical 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 showed that tris-(p-nitrophenyl)phosphate undergoes a cleavage reaction following the initial reduction step.

Results

Voltammetric Methods. Triphenylphosphine. Polargraphic 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 (see) (Figure 1a). Tomes criterion for reversibility, $E_{1/2} - E_{1/4}$, 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$^2$), indicating a diffusion-controlled process. At 3$^o$ the half-wave potential was -2.69 V vs. sce and $E_{1/2} - E_{1/4}$ was 56 mV. Based on the polargraphic results and assuming n = 1, the diffusion coefficient of TPP is calculated to be $0.54 \times 10^{-6} \, \text{cm}^2/\text{sec}$ at 25$^o$ and $0.24 \times 10^{-5} \, \text{cm}^2/\text{sec}$ at 3$^o$.4


8 This value differs significantly from that calculated from the $I_d$ value given by Wawzonek and Wagenknecht, 0.18 x 10$^{-4}$ cm$^2$/sec (25$^o$) under similar conditions. However, in the calculation of this $I_d$ value, the dme values of $m$ and $r$ used were those obtained at open circuit in distilled water (J. H. Wagenknecht, private communication, May 1967). Since the interfacial tension, $\sigma$, between mercury and the solution is smaller for DMF than for water (e.g., at the electropotential maximum, $\sigma_{ho} = 470$ dynes/cm and $\sigma_{ho} = 376$ dynes/cm$^2$), the $m$, which is proportional to $\sigma$, will be smaller in DMF. Moreover, $r$ is much smaller at the very negative potentials of the polargraphic 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 $r$ values extant at the conditions at which $I_d$ is measured. Our value for the diffusion coefficient of TPPO differs from that given in ref 2.


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

<table>
<thead>
<tr>
<th>Sweep rate, mV/sec</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}$ $\mu$A</th>
<th>$i_{pa}/i_{pa}$</th>
<th>$E_{pa}$ V vs. sce</th>
<th>$E_{pa}$ V vs. sce</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without Proton Donor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.1</td>
<td>5.3</td>
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<td>0.90</td>
<td>-2.75</td>
<td>-2.68</td>
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<tr>
<td>130</td>
<td>7.8</td>
<td>9.0</td>
<td>0.97</td>
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<td>-2.68</td>
</tr>
<tr>
<td>222</td>
<td>9.1</td>
<td>11.0</td>
<td>1.01</td>
<td>-2.75</td>
<td>-2.68</td>
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<td>11.2</td>
<td>12.9</td>
<td>0.99</td>
<td>-2.75</td>
<td>-2.68</td>
</tr>
<tr>
<td>867</td>
<td>13.4</td>
<td>15.7</td>
<td>1.00</td>
<td>-2.76</td>
<td>-2.68</td>
</tr>
<tr>
<td>712</td>
<td>15.6</td>
<td>18.4</td>
<td>1.06</td>
<td>-2.76</td>
<td>-2.66</td>
</tr>
<tr>
<td>222</td>
<td>20.0</td>
<td>20.0</td>
<td>1.00</td>
<td>-2.75</td>
<td>-2.68</td>
</tr>
</tbody>
</table>

With Proton Donor

222 86.0 ... ... ... -2.76 ... ...

222 142.0 ... ... ... -2.82 ...

* Estimated by using extrapolation of cathodic current as base line. * Calculated using Nicholson's semiempirical method to obtain $I_{pa}$. * The solution contained 0.1 M TBAI and 0.59 mM TPP in DMF. The working electrode was hmde. Auxiliary electrode was silver wire. Potentials vs. sce may include some uncompensated iR drop. * The concentration of TPP was 2.28 mM. * The solution contained 2.28 mM TPP and 0.014 M hydroquinone. * This solution contained 2.28 mM TPP and 0.03 M hydroquinone.

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


Santhanam, Bard | Electroreduction of Triphenylphosphine
is constant and near one. The current function (proportional to $i_p/n^{1/2}$) 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 nm, while in DMF, only an absorption maximum at 260 nm, which is also reported for TPP in ethyl alcohol, was observed. 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 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. 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. Polargraphic reduction of a solution of TPPO in DMF containing 0.1 $M$ TBAI gives two reduction waves with $E_1/n$ values of $-2.51$ and $-2.84$ V vs. sce (Figure 1b). The wave height of both waves varied with $n^{1/2}$. The difference, $E_1/n - E_1/n^1$, 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 $2.35 \times 10^{-6}$ cm$^2$/sec.

The cyclic voltammetry at a hmdc 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 $i_{pc}/i_{pc}$ 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.

**Table II. Cyclic Voltammetric Data for the Reduction of Triphenylphosphine Oxide**

<table>
<thead>
<tr>
<th>Sweep rate, mV/sec</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$i_{pc}$ $\mu$A</th>
<th>$E_{pc}$, V</th>
<th>$E_{pc}$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>67.1</td>
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<td>44.8</td>
<td>-2.60</td>
<td>-2.52</td>
</tr>
<tr>
<td>312</td>
<td>48.0</td>
<td>51.8</td>
<td>-2.60</td>
<td>-2.52</td>
</tr>
<tr>
<td>476</td>
<td>56.2</td>
<td>60.0</td>
<td>-2.60</td>
<td>-2.52</td>
</tr>
<tr>
<td>714</td>
<td>65.0</td>
<td>70.0</td>
<td>-2.60</td>
<td>-2.52</td>
</tr>
</tbody>
</table>

$^a$ The solution contained 0.1 $M$ TBAI and 3.14 mM 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 semiepiphenolic method $^{10}$ to obtain $i_{pc}$.
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 for biphenyl, \(1.20 \times 10^{-5}\) 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 nm. 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 nm, 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 nm 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 observed 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 nm.

**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

\[
(C_6H_5)_3P + e^{-} \rightarrow (C_6H_5)_3P^-
\]

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.

\[
(C_6H_5)_3P^+ \rightarrow (C_6H_5)_3P^+ + C_6H_6^+ + S^-
\]

Diphenyl phosphinic acid is probably formed during the workup of the electrolyzed solution. Diphenylphosphine is 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, \(^{11}\) 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 \(^3\) that TPP and TBAI react in DMF to form triphenyl-\(n\)-butyl phosphonium iodide. We have found no evidence for this reaction at room temperature during our experiments. Since triphenyl-\(n\)-butyl phosphonium 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.

\[
(C_6H_5)_3P + H^- \rightarrow (C_6H_5)_3P^-
\]

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

---

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

$$(\text{C}_2\text{H}_5)_3\text{PO} + e \rightarrow (\text{C}_2\text{H}_5)_3\text{PO}^-$$

(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 reaction 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. A multipurpose


Reactions of He$^+$ Ions with Gaseous Hydrocarbons.

II. Methane and Ethane

**Fulvio Cacace, Romano Cipollini, and Giovanna Ciranni**

*Contribution from Centro Nazionale di Chimica delle Radiazioni e Radioelementi del C.N.R., Istituto di Chimica Farmaceutica dell'Università, Rome, Italy. Received September 19, 1967*

**Abstract:** The reactions of the He$^+$ 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$^+$ exothermically protonate the methane, giving excited CH$_4$H$^+$ 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$^+$ ions with ethane yields excited C$_2$H$_5$H$^+$ ions, which appear to decompose into labeled ethyl ions, without any appreciable stabilization. The thermoneutral hydride ion transfer from the C$_2$H$_5$ 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$_3^+$, He$^+$, and CH$_3$CHO$^+$, etc., 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, it was shown that, under suitable experimental conditions, the $\beta$ decay of molecular tritium affords a convenient means of producing a very reactive protonating reagent, the He$^+$ 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$^+$ 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. The outlet of the column was connected to a 25-m flow ionization chamber, whose current was measured with an electrometer (Model