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Voltammetric Behavior of Triphenylphosphine in Acetonitrile at a Glassy Carbon Electrode: A Reinvestigation

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Cyclic voltammetry of Ph_3P (**1**) in MeCN at a glassy carbon electrode showed two closely located anodic peaks. The first anodic peak corresponds to the oxidation of **1** to give $Ph_3P=O$ and Ph_3PH^+ (**2**), where water contaminating the medium is the source of the oxygen and the proton. The second peak, which was depressed by an increase in voltage sweep rate, is suggested to involve the oxidation of **1** preceded by a slow deprotonation of **2** formed at the first anodic peak.

Keywords——triphenylphosphine; triphenylphosphonium perchlorate; electrochemical oxidation; cyclic voltammetry; glassy carbon electrode

Voltammetric oxidation of Ph_3P (**1**) in MeCN has been studied by several investigators.[1-3] Schiavon *et al.*[1] has elucidated the electrode process at a Pt electrode in nominally anhydrous MeCN, where the initially generated radical cation, $Ph_3P^{+\cdot}$, reacts with a trace amount of water contaminating the medium and/or with the unoxidized form of **1** to afford $Ph_3P=O$ and $Ph_3P^+\text{-}C_6H_4\text{-}PPh_2$, respectively (Eqs. 1 and 2): the formation of the latter phosphonium ion is appreciable at high concentrations of **1** ($>10^{-2}$ M).

$$3Ph_3P\ (\mathbf{1})+H_2O \longrightarrow Ph_3P=O+2Ph_3PH^+\ (\mathbf{2})+2e \quad (1)$$

$$3Ph_3P \longrightarrow Ph_3P^+\text{-}C_6H_4\text{-}PPh_2+Ph_3PH^+ +2e \quad (2)$$

In both reactions, the apparent number of electrons consumed per molecule of **1** are 2/3, and hence the voltammetric oxidation peak of **1** has been ascribed to a 2/3-electron wave. No voltammetric peak due to further oxidation of Ph_3PH^+ (**2**) has been observed. Similar results were reported at a glassy carbon (GC) electrode.[3] However, in our studies on the reactions of $Ph_3P^{+\cdot}$ with nucleophiles such as dialkyldisulfides[4] and 1,3-dicarbonyl compounds[5] in the presence of $HClO_4$, results were obtained which suggest that **2** is oxidized at a potential close to that for the oxidation of **1**. So, we reinvestigated the cyclic voltammetry of **1** in MeCN at a GC electrode to obtain a more accurate view of the overall process in the electrolysis of **1** in the presence of the nucleophiles described above.

Experimental

Cyclic voltammetry was carried out with the combination of a Hokuto Denko HR-101B potentiostat/galvanostat, a Fuso HECS 321B potential sweep unit, and a Rikadenki RW-21 X-Y recorder. Voltammograms were obtained with a three-electrode system consisting of a GC or Pt working electrode, a Pt wire counter electrode, and a saturated calomel reference electrode (SCE) separated by an agar bridge. The fabrication of the GC electrode has been described previously,[6] and the Pt electrode was fabricated by the same procedure. The phosphine **1** was recrystallized from hexane, and $NaClO_4$ was recrystallized from 95% EtOH and stored over P_2O_5. Ph_3PHClO_4 was prepared by adding a 70% solution of $HClO_4$ (2.2 g) to **1** (2 g) in MeCN (10 ml), then recrystallized from MeCN–ether, and stored over P_2O_5. MeCN was purified by the method of Kiesele.[7]

Results and Discussion

On cyclic voltammetry at a Pt working electrode, **1** showed a single anodic peak at 1.13 V *vs.* SCE in nominally anhydrous MeCN[8] (Fig. 1B). Upon reversal of the sweep direction, a cathodic peak was observed at −0.08 V. These results are consistent with those reported by Schiavon *et al.*,[1] who assigned the cathodic peak to the reduction of **2** formed at the anodic peak. At a GC working electrode, on the other hand, two closely located anodic peaks were observed at 0.98 and 1.13 V (Fig. 1A). No cathodic peak appeared on the reverse sweep before the discharge of dissolved oxygen, probably because the hydrogen over-potenital of a GC electrode is higher than that of a Pt electrode. The peak current (i_p) of the 1st anodic peak varied in proportional to the concentration of **1**, at least in the range of 1 to 10 mM. The potential of the 2nd anodic peak coincided with that of Ph_3PHClO_4, which showed a single irreversible peak under the same conditions (see Fig. 5A), indicating that the peak is attributed to the oxidation of **2** produced at the 1st anodic peak (see Eq. 1). The 2nd anodic

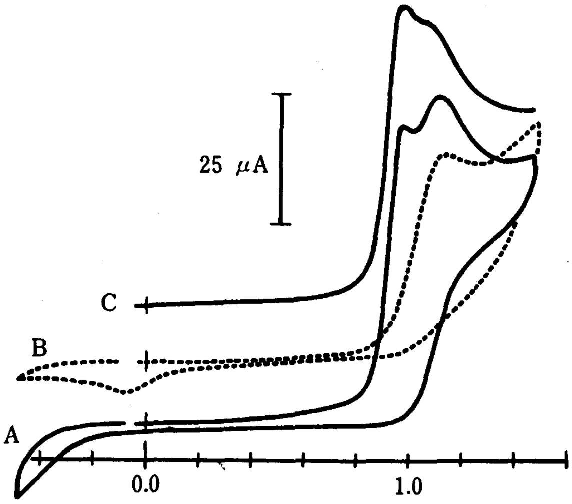

Fig. 1. Cyclic Voltammograms of **1** (4.0 mM)

In MeCN (0.1 M $NaClO_4$) (A) at a GC electrode (geometric area, 0.071 cm^2), (B) at a Pt electrode (geometric area, 0.071 cm^2), (C) see text: voltage sweep rate, 100 mV/s; at 27 °C.

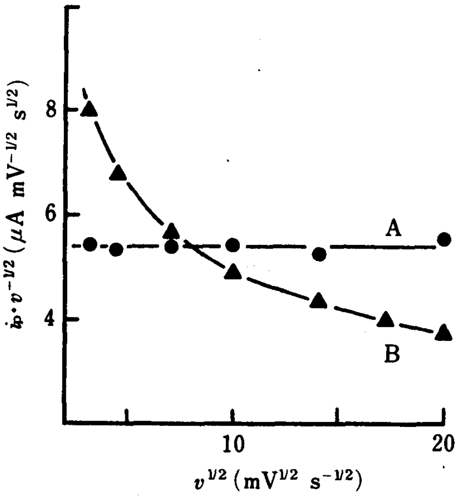

Fig. 2. Effects of Voltage Sweep Rate on the Peak Current of (A) **1** (4.0 mM) and (B) Ph_3PHClO_4 (4.0 mM)

In MeCN (0.1 M $NaClO_4$) at a GC electrode and at 27 °C.

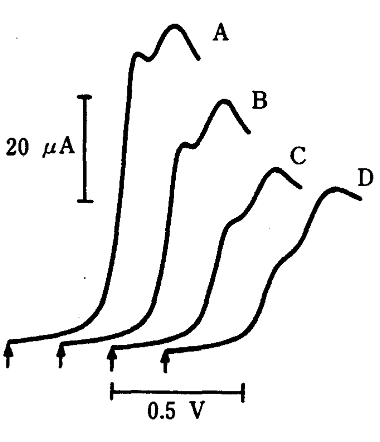

Fig. 3. Effects of Voltage Sweep Rate on the Voltammogram of **1** (4.0 mM)

Voltage sweep rate: (A) 100, (B) 50, (C) 20, and (D) 10 mV/s. In MeCN (0.1 M $NaClO_4$) at a GC electrode and at 27 °C; the potential indicated by an arrow is 0.5 V *vs.* SCE. The curves for the reverse sweep are omitted for simplicity.

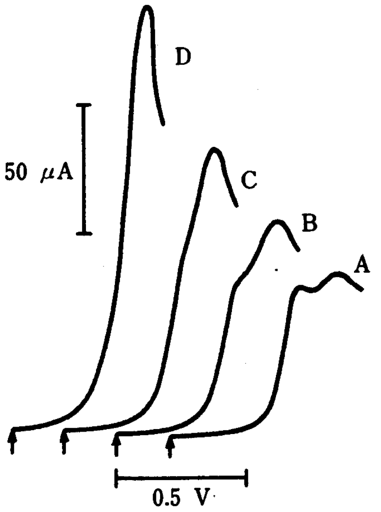

Fig. 4. Cyclic Voltammograms of **1** (4.0 mM)

In MeCN (0.1 M $NaClO_4$) (A) without an additive, (B) with 40 mM and (C) 200 mM H_2O, and (D) with 1100 mM H_2O and 86 mM 2,6-lutidine: at a GC electrode and at 27 °C; voltage sweep rate, 100 mV/s. The potential indicated by an arrow is 0.5 V *vs*. SCE.

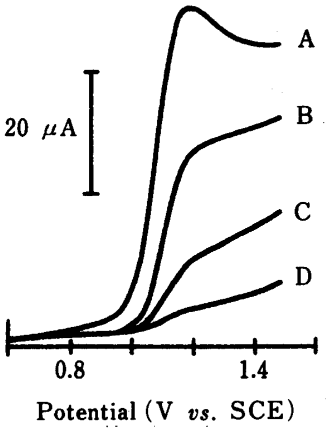

Fig. 5. Cyclic Voltammograms of Ph_3PHClO_4 (4.0 mM)

In MeCN (0.1 M $NaClO_4$) (A) without an additive, and (B) with 20 mM, (C) 80 mM, and (D) 400 mM $HClO_4$; at a GC electrode and at 27 °C; voltage sweep rate, 100 mV/s: 70% $HClO_4$ was used as the source of the acid.

peak was sensitive to atmospheric moisture. Thus, the peak was obscure when the voltammogram was measured in freshly distilled MeCN (Fig. 1C); however, after the solution for the measurement had been allowed to stand for *ca*. 30 min in contact with air, essentially the same voltammogram as shown in Fig. 1A was obtained. It is not clear at present why the protonated phosphine **2** does not give a distinct anodic peak at a Pt electrode.

Further voltammetric measurements on **1** and **2** at the GC electrode were carried out under various conditions (Figs. 2—5).[9] As shown in Fig. 2, the plot of $i_p/v^{1/2}$ *vs*. $v^{1/2}$ for the 1st anodic peak of **1**, where v represents the voltage sweep rate, gave a horizontal straight line, indicating that the electrode process is diffusion-controlled as suggested before at a Pt electrode[1]; that is, the process shown in Eqs. 1 and/or 2 is almost completed within the time scale of the voltammetric measurements examined. In this case, the second anodic peak decreased with v (Fig. 3). In contrast to the 1st anodic peak of **1**, the relation between $i_p/v^{1/2}$ and $v^{1/2}$ for the anodic peak of **2** exhibited a distinct curvature (Fig. 2B).

The effects of additives on the anodic peaks of **1** and **2** were examined. In the presence of added water, the 2nd anodic peak of **1** increased and shifted toward less positive potentials, while the 1st peak remained almost unchanged (Fig. 4). Thus, with a sufficient amount of water (*ca*. 100 mol eq to **1**) the two peaks eventually merged into a single peak (not shown). When 2,6-lutidine, which acts as a base but hardly as a nucleophile,[10] was added along with water, the 1st peak also increased, and in the presence of a large excess of the base and water the height of the merged peak reached a limiting value, which is nearly 3 times that of the original 1st anodic peak (Fig. 4D). Under these conditions the proton liberated at the electrode will be accepted by the base in the place of **1**, and the overall electrode process will be given by Eq. 3, which represents a two-electron process.[11]

$$Ph_3P + H_2O + 2(\text{base}) \longrightarrow Ph_3P{=}O + 2(\text{base})H^+ + 2e \qquad (3)$$

As can be seen in Fig. 5, the anodic peak of **2** was depressed by the addition of $HClO_4$ and almost disappeared with a large excess of the acid. These results, together with the effects of v on i_p (Fig. 2B), suggest that the process giving the anodic peak of **2** is initiated by a slow deprotonation of **2** to **1** followed by electron transfer from the latter to give $Ph_3P^{+\cdot}$.[12]

Water contaminating the medium will act as a base to cause the deprotonation. The decrease of the 2nd anodic peak of **1** with v and the depression of the peak in freshly distilled MeCN are consistent with the proposed reaction process. Under the conditions where the 2nd anodic peak is observed, the concentration of water at the electrode surface must be smaller than in the bulk of the solution, because a part of the water in the immediate neighborhood of the electrode will be consumed in the oxidation of **1** at the 1st anodic peak. Thus, the effects of v on the 2nd peak will be amplified as compared to those on the anodic peak of **2**: the apparent peak height of the 2nd anodic peak of **1** decreased with an increase in v (Fig. 3), whereas that of the anodic peak of **2** did not. The slow deprotonation of **2** is also supported by the observations that Bu_3P, which is a stronger base than **1**,$^{13)}$ showed only one anodic peak on cyclic voltammetry in MeCN at the GC electrode, and that Bu_3PHClO_4 showed no anodic peak before the discharge of the background.

The results described so far might be trivial from the electrochemical viewpoint. However, the fact that electrochemical oxidation of **1** takes place at relatively low potentials even in acidic conditions is significant when the synthetic application of the reactions of $Ph_3P^{+\cdot}$ with various nucleophiles is considered.

References and Notes

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8) The solvent used for the measurements was that purified by the method of Kiesele (ref. 7) and stored in a stoppered bottle for 1 to 7 d, unless otherwise stated.
9) Ph_3PHClO_4 was used as the source of **2**.
10) V. D. Paeker and L. Eberson, *Tetrahedron Lett.*, **1969**, 2839.
11) Controlled potential electrolysis (general procedure, see ref. 6) of **1** in MeCN containing excess water (1.1 M) and 2,6-lutidine (86 mM) gave $Ph_3P=O$ almost quantitatively.
12) The fate of the radical cation will be essentially the same as that of the same species generated directly from **1**: in the controlled potential electrolysis of Ph_3PHClO_4 in MeCN at 1.1 V, no product other than $Ph_3P=O$ was recognized. In Fig. 2, the i_p values for **2** at small v values were larger than those for **1**. This may be attributed to the difference in the amount of water contaminating the medium, though participation of some unknown reactions of $Ph_3P^{+\cdot}$ in the oxidation of **2** cannot be rigorously ruled out.
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