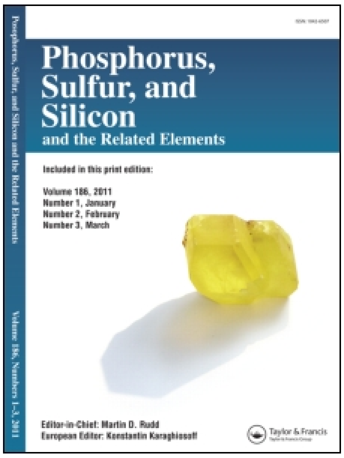

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THE CHEMISTRY OF HETEROARYLPHOSPHORUS COMPOUNDS. PART XII.[1] THE DIFFERENTIAL-PULSE POLAROGRAPHIC REDUCTION OF HETEROARYL- AND HETEROARYLMETHYLPHOSPHONIUM SALTS

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The polarographic reduction of series of heteroaryl- and heteroarylmethylphosphonium salts has been studied using a differential pulse polarographic technique, this having a number of advantages over classical dc polarography. For the salts $Ar_3P^+CH_2PhBr^-$, the observed order of ease of reduction correlates with the electron-withdrawing ability of the heteroaryl group (i.e. Ar = 2-furyl > 2-thienyl > phenyl > 1-methylpyrrol-2-yl). In contrast, for the salts $Ph_3P^+CH_2ArBr^-$ (Ar = 2-furyl, 2-thienyl, phenyl, 1-methylpyrrol-2-yl, 3-thienyl and 3-furyl), the ease of reduction correlates best with the order of stability of the forming carbanions as established in earlier studies of the alkaline hydrolysis of these salts.

INTRODUCTION

The polarographic reduction of quaternary phosphonium salts has received considerable attention in recent years, as preparative electrochemical methods in organophosphorus chemistry have developed.[2–20] Phosphonium salts readily undergo polarographic reduction at the dropping mercury electrode and large scale electrolyses have been utilized for the preparation of optically active phosphines, particularly from benzylphosphonium salts, the benzyl group being cleaved readily from phosphorus.[3,4]

In the polarographic reduction of phosphonium salts, several waves may be observed, making interpretation difficult. The more positive waves are due to the reduction of the phosphonium salts to tertiary phosphines, and the more negative waves are associated with the further reduction of the latter. It is well known that for an irreversible process, the value of the half-wave potential depends markedly on the experimental conditions, and thus it is necessary to standardize the conditions for the series of phosphonium salts under investigation in order that a meaningful correlation of the ease of reduction with the nature of the substituents at phosphorus might be made.[12]

The nature of the processes occurring in the reduction of the phosphonium ion is not completely clear; Horner and Haufe[12] have suggested the following scheme involving successive, related, one electron reduction steps, the group cleaved from phosphorus being lost either as a carbanion or a radical.

$$\begin{tikzcd}
R_4P^+ \arrow[r, "+e"] & R_4P\cdot \arrow[r, "+e"] \arrow[d] & R_4P^- \arrow[d] \\
& R_3P + R\cdot \arrow[r, "+e"] \arrow[d] & R_3P + R^- \arrow[d] \\
& R_3P + \tfrac{1}{2}(R{-}R) & R_3P + RH
\end{tikzcd}$$

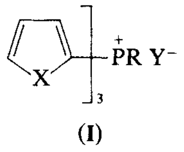
However, as yet no radical-derived products have been observed in the electrolytic reduction of phosphonium salts under aqueous conditions. For example, benzyltriphenylphosphonium bromide, on electrolysis at a mercury cathode, gives triphenylphosphine and toluene in high yield; bibenzyl is not observed.[6,9]

As an alternative to the above, it is possible that the phosphonium ion may undergo a simple, two-electron reduction to eject a carbanion, which then undergoes protonation in aqueous media to form the related hydrocarbon and hydroxide ion. The latter then causes alkaline hydrolysis of unreduced phosphonium ion with formation of phosphine oxide. Thus the electrochemical reduction of the tetraphenylphosphonium ion results in the formation of benzene, triphenylphosphine and triphenylphosphine oxide.[16]

Recent studies of the electrochemical reduction of phosphonium ions in media of low proton availability have shown that a highly complex situation prevails. Under these conditions, both ylide formation and the formation of products derived from radical cleavage of the phosphonium ion have been observed.[21]

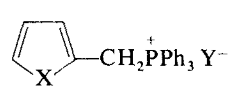
The ease of reduction of a series of salts of the type $Ph_3P^+R\ Br^-$, studied under identical conditions in aqueous solution, depends markedly on the nature of the group R. As the ability of R to stabilize a negative charge (or a radical) increases, the half-wave potential for the reduction process becomes more positive thus reflecting the increasing ease of fission of a phosphorus to carbon bond in the reduction process.[12]

We have recently reported studies of the alkaline hydrolysis of a series of phosphonium salts (**I–III**) bearing heteroaryl- or heteroarylmethyl-substituents.[22,23]



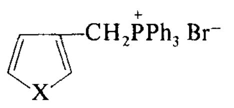
(I)

X = O, S, or NMe
R = Me or $PhCH_2$



(II)

X = O, S, or NMe



(III)

X = O or S

Alkaline hydrolysis of phosphonium salts also proceeds with fission of a phosphorus-to-carbon bond to form a phosphine oxide and a hydrocarbon, the group lost from phosphorus being that which is the most stable as a carbanion. The hydrolyses of the salts (**I**) and (**II**) (X = O or S) are unusual in that they proceed very much more rapidly than their phenyl or benzyl analogues. These observations have been interpreted in terms of the electron-withdrawing effect of the heteroaryl substituent, and the greater stability of the heteroaryl or heteroarylmethyl carbanions, as compared to the phenyl or benzyl carbanions. Since the hydrolysis reaction involves fission of a bond between phosphorus and the heterocyclic substituent, we thought it of some interest to investigate the polarographic reduction of some of these salts in order to ascertain the effects of such heteroaryl substituents on the ease of electrochemical reduction of phosphonium salts.

Many of the studies of phosphonium salt reduction have employed a conventional polarographic technique in which the reduction of the phosphonium ion is carried out in the presence of an appropriate supporting electrolyte which also contains a substance capable of suppressing the polarographic maxima so commonly encountered. Horner and Haufe[12] found it necessary to use as maximum suppressor triton X-100 at a concentration of 0.03–0.05% in their studies of phosphonium salt reduction. We have used similar conditions in a preliminary study of the reduction of the salts (**I–III**) and found that the maxima were not always eliminated with consequent difficulties in the accurate determination of the half-wave potential ($E_{1/2}$). Meites[24] has advised against the use of Triton X-100 at concentrations greater than 0.04% as it can have unusual effects on the polarographic system. It is widely recognized that the indiscriminate use of maximum suppressors may lead to a shift in $E_{1/2}$.

Modern polarographic instrumentation incorporates a potentiostat to control the potential at the working electrode (mercury drop)–solution interface. This can eliminate errors arising from solution resistances and the consequent contribution to resultant voltage drops. Potentiostatic control is accomplished by the introduction of a third electrode. Thus the cell contains three electrodes: the working electrode (dropping mercury electrode); the reference electrode (in this case a saturated calomel electrode connected via a salt bridge) and a counter electrode (a platinum wire in contact with the mercury pool). The working and reference electrodes are connected in a circuit which draws essentially no current, and in this circuit the working potential at the mercury drop can be measured accurately. The current in the cell is measured between the working and counter electrodes.

A recent development in voltammetric analysis is the advent of differential pulse polarography (DPP). In DPP a fixed-height potential pulse is superimposed on the conventional dc voltage ramp. This pulse is synchronized with the end of drop life and the current sampled immediately before the pulse is applied and at the end of the pulse life-time. The difference between these two signals is amplified and presented to the recorder. The polarographic data is thus presented as a series of peaks with maxima at $E_{1/2}$. This greatly simplifies the measurement of $E_{1/2}$ particularly in systems where more than one reduction step is encountered. DPP is also claimed to eliminate the problems arising from polarographic maxima. For these reasons DPP has recently been investigated for a number of applications of organic polarography.[25] In particular it would seem that DPP allows more accurate and precise measurement of $E_{1/2}$ to be made and accordingly we have used the technique to study the polarographic reduction of the salts (**I–III**).

RESULTS AND DISCUSSION

The polarographic reduction of a series of phosphonium salts was investigated using both direct current polarography (with three electrodes) and differential pulse polarography. Figure 1 shows the dc polarographic reduction of benzyltriphenylphosphonium bromide. Severe interference from a polarographic maximum is clearly evident as is the relative difficulty in measuring $E_{1/2}$. Figure 2 shows the reduction of the same compound by DPP. $E_{1/2}$ can in this case be easily measured and the maximum, although still present as a second rather irregular peak, does not interfere with the measurement of $E_{1/2}$ in any way.

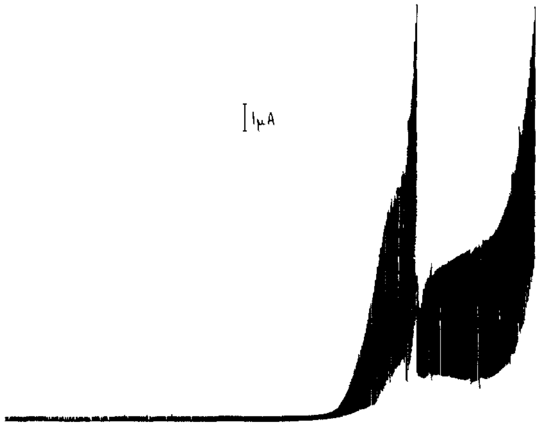


FIGURE 1 Direct current polarographic reduction of benzyltriphenylphosphonium bromide (10^{-3} mol l^{-1}, at pH 7.0).

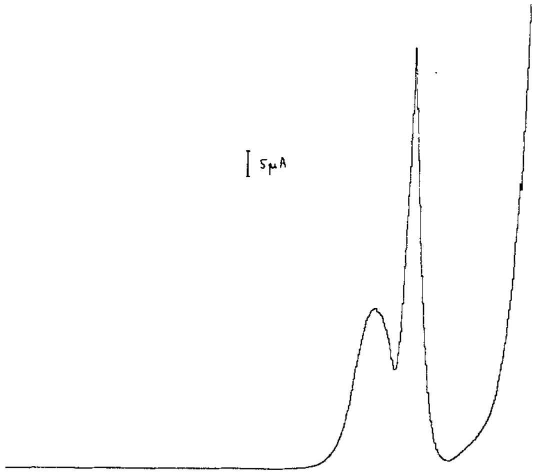


FIGURE 2 Differential pulse polarographic reduction of benzyltriphenylphosphonium bromide (10^{-3} mol l^{-1}, at pH 7.0).

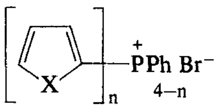
TABLE I

Differential pulse polarographic reduction of the salts $Ar_3P^+CH_2PhBr^-$ (10^{-3} mol. l^{-1}) in aqueous solution at pH 7.00

Phosphonium salt	$E_{1/2}$ (*vs.* SCE)
Ar = 2-furyl	−1.415 ± 0.003
Ar = 2-thienyl	−1.474 ± 0.003
Ar = phenyl	−1.700 ± 0.003
Ar = 1-methylpyrrol-2-yl	−1.938 ± 0.003

The observed half-wave potentials for the differential pulse polarographic reduction at pH 7.0 of the salts (**I**, X = O, S or NMe; R = CH_2Ph), together with that of benzyltriphenylphosphonium bromide are given in Table I. $E_{1/2}$ values are recorded relative to the standard calomel electrode (SCE). The potential recorded corresponds to the first (i.e. most positive) reduction wave observed.

There is thus a marked dependence of $E_{1/2}$ on the nature of the heteroaromatic system attached to phosphorus, the ease of reduction decreasing in the order 2-furyl > 2-thienyl > phenyl > 1-methylpyrrol-2-yl. Horner *et al*[17] have similarly shown that in a series of tetraarylphosphonium salts of type (**IV**), the 2-furyl- and 2-thienyl-containing salts undergo reduction more easily than tetraphenylphosphonium bromide. Large scale electrolysis studies of these salts in methanol have also shown that the heteroaryl substituents are cleaved from phosphorus in preference to phenyl.



(**IV**), X = O or S

The above order of half-wave potentials can best be correlated with the electron-withdrawing effects of the heteroaryl substituents as indicated by the pK_a data for the corresponding 2-heteroarylcarboxylic acids.[26,27] Thus furan-2-carboxylic acid and thiophen-2-carboxylic acid are stronger acids than benzoic acid, whereas pyrrole-2-carboxylic acid is weaker. It is of interest that the relative ease of reduction does *not* correlate with the order of

TABLE II

Differential pulse polarographic reduction of the salts $Ph_3P^+CH_2Ar$ X^- (10^{-3} mol. l^{-1}) in aqueous solution at pH 7.00

Phosphonium salt	$E_{1/2}$ (*vs.* SCE)
Ar = 2-furyl X = Br^-	−1.675 ± 0.005
Ar = 2-thienyl X = Br^-	−1.675 ± 0.002
Ar = 1-methylpyrrol-2-yl X = I^-	−1.751 ± 0.003
Ar = phenyl X = Br^-	−1.700 ± 0.003
Ar = 3-thienyl X = Br^-	−1.715 ± 0.001
Ar = 3-furyl X = Br^-	−1.840 ± 0.003

stability of the forming 2-heteroaryl carbanions, established in our earlier studies of alkaline hydrolysis to be 2-thienyl > 2-furyl > 1-methylpyrrol-2-yl > phenyl.[23] Thus it is possible that in this series of phosphonium salts, the first reduction wave corresponds mainly to the addition of an electron to the phosphorus of the phosphonium ion to form a phosphoranyl radical, Ar_3PCH_2Ph, this process being increasingly favoured as the electron-withdrawing ability of the substituents increases. We have suggested that the position of the pre-equilibria between related heteroarylphosphonium ions and hydroxide ion (resulting in the formation of hydroxyphosphoranes) in the alkaline hydrolysis of phosphonium salts can also be related to the above order of relative electron-withdrawing power of the substituents.[23]

We have also studied the polarographic reduction of a number of salts of types (**II** and **III**) bearing heteroarylmethyl groups, and the half-wave potentials are listed in Table II.

Although the heteroaryl substituent is now not directly attached to phosphorus, there is still a noticeable dependency of the half-wave potential on the nature of the heteroarylmethyl group. From our studies of the rate and course of alkaline hydrolysis of this series of salts,[22,23,28] we have concluded that the relative stabilities of the forming heteroarylmethyl carbanions are in the order 2-furylmethyl > 2-thenyl > benzyl > 1-methylpyrrol-2-yl and benzyl > 3-thenyl > 3-furylmethyl. The relative carbanionic stabilities of the 1-methylpyrrol-2-yl carbanion and the 3-heteroarylmethyl carbanions have not been established so far. These orders of carbanionic stability correlate reasonably well with the order of polarographic reduction of the above salts. Thus the 2-furylmethylphosphonium salt is the most easily reduced and the 3-furylmethyl analogue the least easily reduced. It is particularly significant that the 3-thenylphosphonium salt is more easily reduced than the 3-furylmethyl analogue. This observation clearly indicates that in the reduction of this series of salts, carbanion formation would seem to be involved in the reduction process responsible for the observed polarographic wave. In addition, as for the alkaline hydrolysis of 3-heteroarylmethylphosphonium salts, the preferential reduction of the 3-thenyl salt points to some sulphur 3*d* orbital involvement in the stabilization of the forming carbanion.

If the above correlation is reasonable, then the polarographic data indicates that the forming 1-methylpyrrol-2-yl carbanion is less stable than the forming 3-thenyl carbanion, but more stable than the forming 3-furylmethyl analogue. We hope to investigate this point further by studying the hydrolysis of mixed heteroarylmethylphosphonium salts bearing these groups.

EXPERIMENTAL

The phosphonium salts were prepared and purified as previously described.[22,23,28]

The polarographic studies were carried out using a Model 174 Polarographic Analyser (Princeton Applied Research) in conjunction with a PAK Servoscribe XY Recorder. The polarographic cell comprised a dropping mercury electrode with a hammer and timer to ensure a drop time of 1 s, a standard calomel electrode as reference, and a platinum wire counter electrode in contact with the discharged mercury at the bottom of the cell. The solutions of the phosphonium salts were prepared at a concentration of 10^{-3} mol l^{-1} in a solution containing "Britton-Robinson buffer" (pH 7.00), which also functioned as the supporting electrolyte, at a concentration of approximately 0.1 mol l^{-1}. No maximum suppressor was used. The solutions were degassed for 10 min before polarography commenced and the polarographic cell thermostated at 25°C.

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