Electrochemical Reduction of Phosphonium Cations in Media of Low Proton Availability

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Received July 7, 1976

The electrochemical reduction of a series of alkyltriphenylphosphonium cations is studied in media of low proton availability as a function of the alkyl group, initial concentration, nature and water content of the solvent, and electrolysis potential. With reference to previous work on Ph_4P^+ and on phosphoniums giving rise to stable ylides, a general picture of the mechanisms is drawn with emphasis on the following points: (1) interference of the starting cation as an acid in the reaction process leading to ylide or phosphine oxide formation and to Hofmann degradation; (2) competition between the two-electron pathway involving the above-mentioned reactions and the one-electron pathway leading to dimerization and/or disproportionation of the initially expelled radical; (3) factors determining the competition between the one-electron and the two-electron pathway and the various reactions inside each of them; (4) orientation of cleavage in electrochemical reduction and phosphine oxide formation.

The polarography and preparative scale electrolysis of a large number of phosphonium cations have been studied in protic media such as water and water–alcohol mixture.[1–9] In these conditions the reduction process results most generally in a hydrogenolysis of the carbon–phosphorus bond

$$R_4P^+ + 2e + H^+ \rightarrow RH + R_3P$$

leading to a hydrocarbon and the corresponding tertiary phosphine. The exceptions to this rule are very few and involve compounds of very particular structure.[10] The main selectivity problem is then the orientation of the reductive cleavage as a function of the groups borne by the phosphorus atom. The orientation appears to be influenced by the nature of the electrode material as shown by comparative studies using mercury, lead, platinum, zinc, and copper.[2]

In media of low proton availability the previous work has essentially been concerned with two opposite types of phosphonium cations. The first group involves cations bearing an hydrogen atom on a carbon α to the phosphorus, hence able to give rise to an ylide. The second series of studies was devoted to the tetraphenylphosphonium in which the formation of an ylide is impossible.

Thus in the reduction of cyanomethyltriphenylphosphonium in dimethyl sulfoxide the formation of the ylide is suggested by the presence on the polarogram of a wave located at the same potential as the wave of the chemically synthetized ylide and by the isolation of triphenylphosphine oxide in the products of preparative scale electrolysis.[11] Wittig reactions have been carried out electrochemically by reducing the methyl-, ethyl-, benzyl-, and carbomethoxymethyltriphenylphosphonium in the presence of carbonyl compounds.[12] However, it is not clear whether the ylide was formed during the reduction of the phosphonium itself or that of the carbonyl compound. More recently a systematic study of phenacyl-, benzhydryl-, and benzyltriphenylphosphonium in acetonitrile (ACN), dimethylformamide (DMF), and hexamethylphosphoramide (HMPA) has shown that the ylide formation resulting from a two-electron reductive cleavage of the starting phosphonium is a quantitative reaction

$$\begin{array}{l} R_2CHP^+Ph_3 + 2e \rightarrow R_2CH^- + PPh_3 \\ R_2CH^- + R_2CHP^+Ph_3 \rightarrow R_2CH_2 + R_2C{=}PPh_3 \\ \hline R_2CHP^+Ph_3 + 1e \\ \qquad \rightarrow 0.5PPh_3 + 0.5R_2C{=}PPh_3 + 0.5R_2CH_2 \end{array}$$

leading to a 50% yield of ylide relative to the starting material with an apparent number of electrons exchanged being equal to 1.[13]

The conclusion of the most recent study[14] of the tetraphenylphosphonium reduction, which discusses previous work on the subject,[6,15,16] is that the main reduction pathway is again a two-electron cleavage, leading, however, to the phosphine oxide instead of the ylide:

$$\begin{array}{c} Ph_4P^+ + 2e + H_2O \rightarrow PPh_3 + PhH + OH^- \\ Ph_4P^+ + OH^- \rightarrow PPh_3O + PhH \\ \hline Ph_4P^+ + 1e + 0.5H_2O \rightarrow PhH + 0.5PPh_3 + 0.5PPh_3O \end{array}$$

The apparent number of electrons is again equal to one, although the electrochemical cleavage is a two-electron process. In this case, however, a minor but distinct competitive pathway is an actual one-electron reaction leading to the formation of diphenyl in a few percent yield. Phosphine oxide and dimers have also been reported in the reduction products of benzyl-, allyl-, and 9-fluorenyltriphenylphosphonium on an aluminum cathode in DMF.[17] However, these results are difficult to interpret since the anodic and cathodic compartments were not separated.

The purpose of the present paper is to report and discuss the results obtained with a series of alkyltriphenylphosphonium cations (RP^+Ph_3) in solvents of low proton availability such as ACN, DMF, and HMPA. The selection of the cations was made in an attempt to discuss the following points: (1) relative efficiency of the one-electron and the two-electron pathway; (2) orientation of the cleavage in the reduction and the phosphine oxide formation as a function of R; (3) involvement of the starting material in other acid–base reactions than ylide and phosphine oxide formation such as Hofmann degradation; (4) formation of alkenes during the reduction either from Hofmann degradation in the two-electron pathway or from H-exchange disproportionation in the one-electron pathway; (5) mechanism of phosphine oxide formation in the case of cations giving unstable ylides; (6) influence of the structure of R, the nature and water content of the solvent, the initial concentration, and the electrolysis potential on the selectivity of the reduction according to the various reaction paths summarized in Table I. This will lead, with reference to the results already obtained with Ph_4P^+ and the cations giving stable ylides, to an overall picture of the phosphonium reduction in media of low proton availability. Three groups of phosphonium cations as shown in Table II were studied.

The electrochemical reduction of CTP, DTP, and ATP has not been studied so far. The reduction of the three other phosphoniums has been investigated in water mostly from a preparative standpoint and in some cases polarographically. BTP electrolysis on mercury yields 50% isobutane, 27% isobutene, 85% PPh_3, traces of benzene, and an unidentified product. [6]The reaction mechanism was not given and it is to

Table I

Initial electrode electron transfer	(1)	$RP^+Ph_3 + 1e \rightleftarrows RP^\cdot Ph_3$		
Competitive radical cleavage	(2)	$RP^\cdot Ph_3 \rightarrow R^\cdot + PPh_3$	$RP^\cdot Ph_3 \rightarrow Ph^\cdot + RPPh_2$	(3)
Dimerization	(4)	$R^\cdot \rightarrow \frac{1}{2}R{-}R$	$Ph^\cdot \rightarrow \frac{1}{2}Ph{-}Ph$	(5)
H-atom transfer disproportionation	(6)	$R^\cdot \rightarrow \frac{1}{2}RH + \frac{1}{2}R(-H)$		
2d electrode electron transfer	(7)	$R^\cdot + 1e \rightleftarrows R^-$	$Ph^\cdot + 1e \rightleftarrows Ph^-$	(8)
2d solution electron transfer	(9)	$R^\cdot + RP^\cdot Ph_3 \rightleftarrows R^- + RP^+Ph_3$	$Ph^\cdot + RP^\cdot Ph_3 \rightleftarrows Ph^- + RP^+Ph_3$	(10)
Hofmann degradation	(11)	$R^- + RP^+Ph_3 \rightarrow R(-H) + RH + PPh_3$	$Ph^- + RP^+Ph_3 \rightarrow R(-H) + PhH + PPh_3$	(12)
Ylide formation	(13)	$R^- + RP^+Ph_3 \rightarrow R(-H){=}PPh_3 + RH$	$Ph^- + RP^+Ph_3 \rightarrow R(-H){=}PPh_3 + PhH$	(14)
Phosphine oxide formation	(15)	$R^- + H_2O \rightarrow RH + OH^-$	$Ph^- + H_2O \rightarrow PhH + OH^-$	(16)
	(17)	$R(-H){=}PPh_3 + H_2O \rightleftarrows RP^+Ph_3 + OH^-$		
	(18)	$RP^+Ph_3 + OH^- \rightarrow PPh_3O + RH$	$RP^+Ph_3 + OH^- \rightarrow RPPh_2O + PhH$	(19)

Table II. Phosphonium Cations

Name	Formula	Abbreviation
Cumyltriphenylphosphonium	$C_6H_5(CH_3)_2CP^+(C_6H_5)_3$	CTP
1,1-Diphenylethyltriphenylphosphonium	$CH_3(C_6H_5)_2CP^+(C_6H_5)_3$	DTP
tert-Butyltriphenylphosphonium	$(CH_3)_3CP^+(C_6H_5)_3$	BTP
tert-Amyltriphenylphosphonium	$C_2H_5(CH_3)_2CP^+(C_6H_5)_3$	ATP
Ethyltriphenylphosphonium	$C_2H_5P^+(C_6H_5)_3$	ETP
Methyltriphenylphosphonium	$CH_3P^+(C_6H_5)_3$	MTP

Table III

	CTP			DTP			BTP		ATP	
Solvent	ACN[a]	DMF[a]	HMPA[b]	ACN[a]	DMF[a]	HMPA[b]	ACN[a]	DMF[a]	ACN[a]	DMF[a]
$-E_{1/2}^{(1)}$	1.510	1.590	1.662	1.240	1.290		1.820	1.710	1.780	1.650
$-E_{1/2}^{(2)}$	2.500	2.550	2.600	2.490	2.530		2.475	2.340	2.395	2.330
$-E_{1/2}^{(3)}$		2.770	2.820		2.750			2.670		2.665
$-E_p^{(1)}$	1.660[c]	1.610[c]			1.340[c]	1.590[c]	1.910[e]	1.800[c]	1.810[d]	1.780[c]
$-E_p^{(2)}$	2.600[c]	2.550[c]			2.500[c]	2.900[c]	2.500[e]	2.440[c]	2.312[d]	2.440[c]
$-E_p^{(3)}$		2.750[c]			2.700[c]	3.100[c]		2.680[c]		2.660[c]

[a] Reference electrode: SCE. [b] Reference electrode: Ag/Ag$^+$ (0.01 N). [c] Sweep rate: 3.5 V s^{-1}. [d] 3.0 V s^{-1}. [e] 0.3 V s^{-1}.

be noticed that the electrode potential was not controlled, electrolysis being carried out at constant current. With ETP, the electrolysis in water yields on mercury 59% $EtPPh_2$, 35% PPh_3, 42% PhH, 7% C_2H_6, 0.04% C_2H_4, and an unidentified product.[2,3,6] On lead the cleavage of the ethyl group is much more predominant (91%). With MTP, 85% $MePPh_2$, 5.5% PPh_3, 82.3% benzene, and 0.34% methane are obtained on mercury.[2,3,6] The ratio of the two phosphines appears to depend upon the electrode material.[2]

Results

The similarities in electrochemical behavior found among the six considered phosphonium leads us to group them in three series of two as shown in Table II.

Polarography–Cyclic Voltammetry (CV)–Coulometry. CTP and DTP. In DMF and HMPA three polarographic waves are observed when the initial concentration is larger than 1 mM l.$^{-1}$. The second and third waves correspond to the reduction of triphenylphosphine oxide and triphenylphosphine, respectively. The potential characteristics of the polarographic waves in ACN with 0.1 N Et_4NClO_4, DMF with 0.1 N Bu_4NI, and HMPA with 0.1 N Bu_4NBF_4 together with those of the cyclic voltammograms obtained at 3.5 V s^{-1} are given in Table III. The second wave is not proportional to the initial concentration C_0 as shown in Figure 1, where the ratio of its height to C_0 is represented as a function of C_0 at 20 and −31 °C. The first wave itself is not proportional to C_0 as shown in Figure 2. At any of these concentrations the apparent number of electrons exchanged is one as determined by coulometry. Addition of a proton donor such as formic acid increases the height of the first wave to an extent depending on the initial concentration. Thus for C_0 = 1 mM l.$^{-1}$ the wave height is multiplied by 1.4 upon addition of 5 mM l.$^{-1}$ formic acid. Addition of more formic acid does not result in a further increase. For C_0 = 5 mM l.$^{-1}$ multiplication by 1.84 is observed in the same conditions. It is noted that the ratio of the wave height over concentration is practically the same in both cases and also the same for the wave without proton donor at C_0 = 0.1 mM l.$^{-1}$ where no PPh_3O wave is observed.

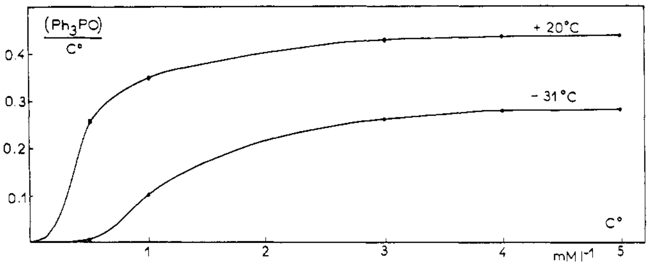

Figure 1. Relative height of the second wave of CTP as a function of initial concentration, in DMF with 0.1 N Bu_4NI as referred to the wave of pure Ph_3PO at the same concentration.

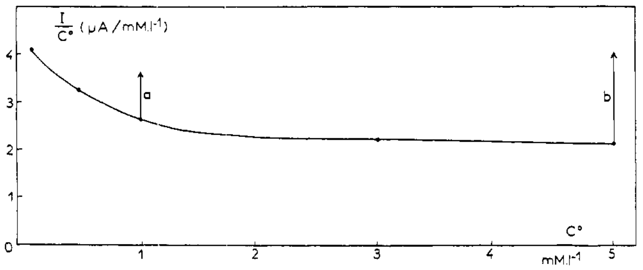

Figure 2. Relative height of the first wave of CTP as a function of the initial concentration in DMF with 0.1 N Bu_4NI at 20 °C. Increase of the height upon addition of (a) 5.3 mM l.$^{-1}$ formic acid; (b) 5 mM l.$^{-1}$ formic acid.

Similar observations are made in ACN with 0.1 N Et_4NClO_4 except that the third wave, corresponding to PPh_3 reduction, cannot be seen before the discharge of the supporting electrolyte. The effect of proton donor addition is of the same type although smaller than in DMF. Again the coulometric number of electrons is one.

In cyclic voltammetry (CV) three waves are observed in DMF and HMPA and two waves in ACN. Their potential characteristics are summarized in Table III. As in the case of Ph_4P^+,[14] the second wave tends to disappear upon raising the sweep rate. However, it has practically disappeared at 21 V s^{-1} for C_0 = 1 mM l.$^{-1}$ whereas for Ph_4P^+ a sweep rate of about 1500 V s^{-1} was required in the same conditions. The sweep rate required for suppressing the second wave increases with C_0; it reaches 1500 V s^{-1} for C_0 = 5 mM l.$^{-1}$.

BTP and ATP. In ACN two polarographic waves of unequal height are observed, the second being approximately one-half of the first. The second wave can neither be assigned to a phosphine oxide PPh_3O or $RPPh_2O$ nor to the alkene R(–H). The polarogram obtained after electrolysis on the first wave does not show any more wave, indicating that the second wave is not assignable to a stable reduction product. Coulometry on the first wave gives a number of electrons equal to one. The same result is found at the potential level of the second wave despite the very existence of this wave. The same observations have been made of the ATP cation.

In DMF with Bu_4NI as supporting electrolyte the behavior of BTP and ATP is essentially the same. A third wave corresponding to the reduction of PPh_3 is now observed. The addition of a proton donor, phenol or formic acid, does not result in any increase of the first wave.

In cyclic voltammetry two waves are observed in ACN with 0.1 N Et_4NClO_4 and three waves in DMF with 0.1 N Bu_4NI for both cations (Figure 3a). The characteristic potentials of the polarographic and CV waves are reported in Table III. The last wave in DMF corresponds to the reversible reduction of PPh_3. The reaction of Bu_4NOH on both cations lead to the quantitative formation of a phosphine oxide resulting from the expulsion of the phenyl group, i.e., *t*-$BuPPh_2O$ and *t*-Amyl-PPh_2O, as shown by comparison of the reversible wave they give in DMF (Figure 3b) with those obtained with authentic samples. We have also prepared these compounds in the same manner in ACN starting from 5–6 g of the initial phosphonium and identified them by NMR and elemental analysis after extraction. No trace of PPh_3O is found in the attack of the phosphonium by OH^-.

Figure 4c and 4d show the voltammograms obtained after electrolysis of BTP in DMF on the first and second wave, respectively. In the first case the only electroactive reduction product is PPh_3. In the second one PPh_3 is again obtained but $RPPh_2O$ is also formed.

ETP and MTP. In ACN the polarogram of ETP exhibits two waves, the second one having the shape of a maximum (Figure 4). The maximum is less pronounced with Bu_4NI as supporting electrolyte than with Et_4NClO_4 (Figure 4). That this phenomenon is related to adsorption of the starting material and self-inhibition can be seen on the cyclic voltammogram (Figure 5) which shows the anodic trace rising above the cathodic curve in the region of the maximum. A third wave is also apparent on the cathodic curve. Mercury seems to play a specific role in the adsorption phenomenon since on platinum an uncomplicated irreversible peak is observed.

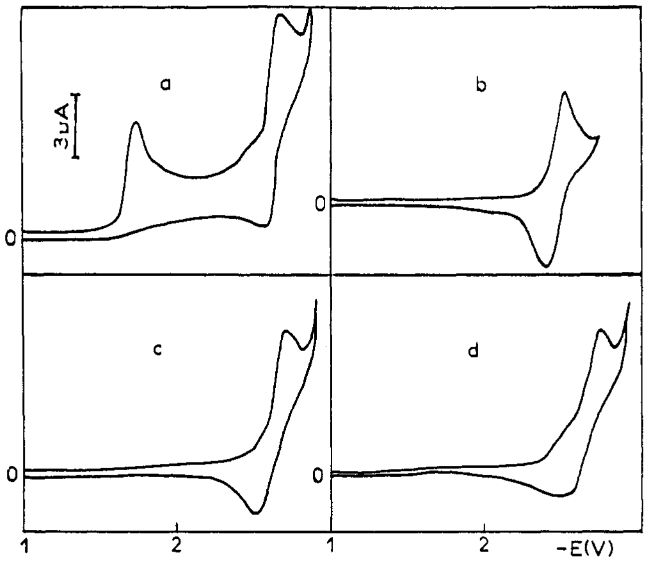

Figure 3. Cyclic voltammetry of *tert*-butyltriphenylphosphonium in DMF with 0.1 Bu_4NI. (a) BTP concn 1 mM l.$^{-1}$. (b) Same solution after treatment by an equimolar quantity of Bu_4NOH. (c) Same solution after electrolysis on the first wave. (d) Same solution after electrolysis on the second wave. Sweep rate: 3.5 V s^{-1}. Reference electrode: SCE.

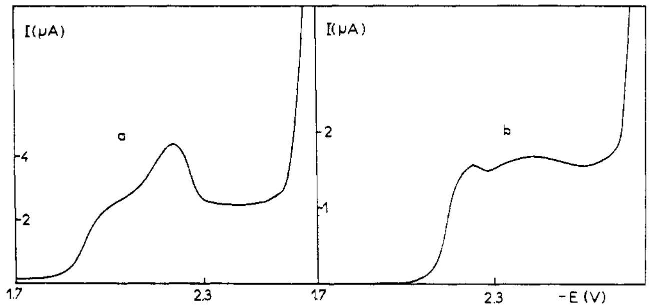

Figure 4. Polarography of 1 mM l.$^{-1}$ ethyltriphenylphosphonium in ACN with (a) 0.1 N Et_4NClO_4; (b) 0.1 N Bu_4NI. Reference electrode: $Ag/Ag^+(10^{-2}$ N).

Similar observations can be made when using DMF and HMPA with 0.1 N Bu_4NI and 0.1 Bu_4NBF_4, respectively. The adsorption phenomenon is less pronounced and four waves are now observed in polarography and CV. The second wave corresponds to the reduction of $EtPPh_2O$, the third to PPh_3, and the fourth to $EtPPh_2$. Doubling of the first wave is obtained upon addition of a proton donor such as phenol. Coulometry on the first wave or on the maximum indicates a number of electrons equal to one.

The behavior of MTP is very similar. Adsorption again interferes in the polarographic and CV patterns although to a lesser extent. Polarography and CV indicate the formation of PPh_3, $MePPh_2$, and $MePPh_2O$ but not of PPh_3O.

Preparative Scale Electrolysis. Two kinds of controlled potential electrolyses, preparative scale and analytical scale, were performed. The first ones, using several grams of starting

Table IV. Analytical Scale Electrolysis of Cumyltriphenylphosphonium. Ratios of Dimerization (α) and Hofmann Degradation (β) as Functions of the Solvent and Initial Concentration

Solvent (water content)	Concn, (mM l.$^{-1}$)	% Ph_3P	% Ph_3PO	% RR	% RH	% R(—H)	α	β
ACN	1	60	40	2.3			0.09	0.16
(0.4%)	25	70	30	13	64	3	0.41	0.19
DMF	10	75.5	24.5	17.9	57	8	0.53	0.23
(0.2%)	25	80	20	24.4	45.6	5.6	0.66	0.33
	50	97	3.5	40	13.5	5.2	0.89	0.69
	55[a]	100	0	45.8	5	5.15	0.96	0.70
(<0.05%)	25	100	0	25.3	23.1	24.4	0.67	1.00
HMPA	50	100	0	24.1	24	25.8	0.65	1.00
(0.2%)	50	100	0	25.2	23	24	0.67	1.00
(0.6%)	50	97.5	5	18	37	26	0.53	0.88
(2%)	50	90	10	16.3	43	24	0.53	0.80

[a] Without supporting electrolyte.

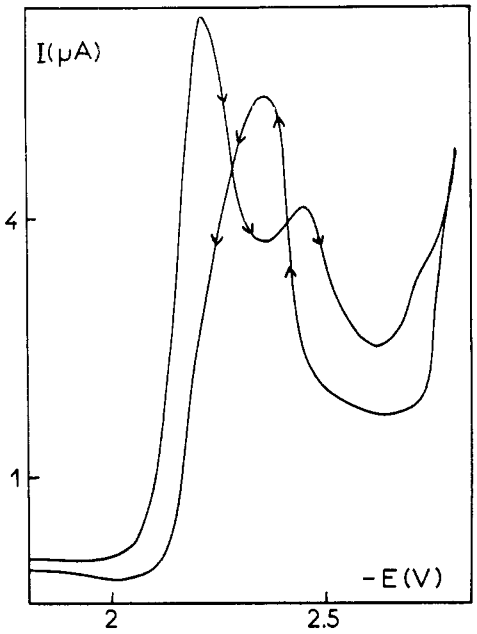

Figure 5. Cyclic voltammetry of 1 mM l.$^{-1}$ ethyltriphenylphosphonium in ACN with 0.1 N Et_4NClO_4. Reference electrode: Ag/Ag$^+$(10^{-2} N). Sweep rate: 0.3 V s^{-1}.

material, were devised for extracting and identifying the electrolysis products and the second, using smaller quantities, for determining the yields in each product by direct analysis of the electrolyzed solution.

CPT and DTP. From the first type of electrolyses carried out at the potential of the first wave the following products, besides PPh_3 and PPh_3O, were identified by NMR and VPC by comparison with authentic samples: in the case of CTP, cumene, dicumene, and α-methylstyrene; in the case of DTP, 1,1-diphenylethane, 2,2,3,3-tetraphenylbutane, and 1,1-diphenylethylene.

There is no trace of phenyl expulsion either in the reductive cleavage or in the phosphine oxide formation.

The results of the analytical scale electrolyses of CTP are given in Table IV as a function of the solvent, the water content, and the initial concentration. Throughout the paper the yield of a given product is defined as the ratio of the mole numbers of the product over the starting material.

Table V. Analytical Scale Electrolysis of *tert*-Butyltriphenylphosphonium

Solvent	Concn, mM l.$^{-1}$	% Ph_3P	% Ph_3PO	% RR	% RPh_2PO
ACN	10	100	0	7.5	0
	50	100	0	4.5	0
DMF	50	100	0	2.5	0

BTP and APT. Preparative scale electrolyses in ACN starting with 3–5 g of phosphonium salts were performed on the first wave. The resulting solutions were shown by extraction with cyclohexane and benzene to contain PPh_3 with a yield close to 100% and no phosphine oxide.

The results of analytical scale electrolysis of BTP on the first wave in ACN and DMF are given in Table V. The yields in PPh_3 and hexamethylethane were determned by VPC by comparison with authentic samples. The very volatile isobutane and isobutene were not titrated. Electrolysis on the second wave results in the formation of t-$BuPPh_2O$, 8% benzene, and 90% PPh_3. Analogous results are obtained with ATP.

ETP and MTP. Analytical scale electrolysis of ETP in DMF with an initial concentration of 50 mM l.$^{-1}$ on the first wave leads to 43% PPh_3, 9% $EtPPh_2$, 45% $EtPPh_2O$, and 57% PhH. Similar results are obtained in the potential region of the maximum and also on a platinum electrode.

In order to get evidence for ylide generation, electrolyses were performed in DMF and HMPA on 1–2 mM solutions with addition of a proton donor after completion of the electrolysis. Partial regeneration of the starting cation was then observed polarographically in both cases. It corresponds to a yield in ylide of 30% in DMF and 78% in HMPA.

Quantitative formation of $EtPPh_2O$ upon attack by OH^- was checked at the millimolar level using CV and at preparative scale by extraction and NMR identification. There is no formation of PPh_3O in this reaction.

In the case of MTP the following yields were obtained in analytical scale electrolysis in the three solvents for a 55 mM l.$^{-1}$ initial concentration:

	% PPh_3	% $MePPh_2$	% $MePPh_2O$	% PhPh
ACN	34	30	38	8
DMF	22	30	50	0
HMPA	33	26	46	1

Reaction of MTP with OH^- results again exclusively in the expulsion of the phenyl group leading to $MePPh_2O$.

The same experiment for detecting the ylide formation in DMF and HMPA as with ETP did not lead to any phosphonium regeneration.

Discussion

CTP and DTP. It may be noted first that the ratio of disproportionation to dimerization for the cumyl radical is only a few percent.[18] Disproportionation can then be practically neglected and therefore it can be considered that the alkene results essentially from Hofmann degradation.[19,20] It can also been assumed that the base involved in this reaction is R^- itself since, as we have checked ourselves, the action of OH^- leads exclusively to PPh_3O and RH. The reaction mechanism can therefore be described as the following combination of reactions from Table I: (1) + (2) + α(4) + $(1 - \alpha)$ [(7) (or 9) + β(11) + $(1 - \beta)$(15–18)], leading to the balance equation

$$\begin{aligned} RP^+Ph_3 + 1e + (1 - \alpha)(1 - \beta)/(2 - \alpha)H_2O \\ \rightarrow [1 + \beta(1 - \alpha)]/(2 - \alpha)PPh_3 + \alpha/2(2 - \alpha)R\text{–}R \\ + (1 - \alpha)(2 - \beta)/(2 - \alpha)RH + \beta(1 - \alpha)/(2 - \alpha)R(\text{–}H) \\ + (1 - \alpha)(1 - \beta)/(2 - \alpha)PPh_3O \end{aligned}$$

α features the relative importance of the one-electron pathway which is here reduced to dimerization; $1 - \alpha$ features the two-electron pathway leading transitorily to R^- and then to Hofmann degradation (β) and phosphine oxide formation ($1 - \beta$). α and β can be derived from the yields in the various products given in the balance equation. The best accuracy is obtained when deriving β from the dimer yield and β from PPh_3 formation. The values of α and β thus determined are shown in Table IV.

In HMPA when no water is purposely added, the Hofmann degradation is practically complete. This can be explained by considering that the direct attack of R^- on the starting phosphonium, rather than on water, is favored by the low water content and by the strong complexation of the water molecule by the solvent. α does not vary with C_0 in HMPA in contrast to what happens in DMF in the same concentration range. Indeed, both dimerization and Hofmann degradation are second-order processes which are likely to be influenced in the same manner by C_0 variations. Addition of water clearly favors reaction 15 leading to PPh_3O through reaction 18. Thus the two-electron route is overall accelerated leading to a decrease of the dimerization rate α.

In ACN and DMF, raising C_0 results in an increase of α and to a lesser extent of β. In the same concentration conditions β is smaller in ACN than in DMF owing to the higher water content and the larger acidic activity of water in the first solvent than in the second one. The one-electron route (reaction 4) is second order whereas the two-electron route possesses a mixed character: first order as regards reaction 15 and second order for reaction 11, the first-order character corresponding to PPh_3O formation being predominant. An increase in C_0 thus favors mostly the one-electron pathway, i.e., the dimer formation, and to a lesser extent the Hofmann degradation as observed experimentally. Comparison of the results obtained in HMPA and DMF at the same concentration, e.g., 50 mM $l.^{-1}$, shows that Hofmann degradation is faster in the first solvent as can be expected from the fact that R^- is probably less solvated. Otherwise the dimer yield should be of the same order in both cases. On these bases the results of polarography and CV can now be interpreted. It is seen from the results of controlled potential electrolysis that, in the millimolar range, dimerization and Hofmann degradation are negligible, the formation of phosphine oxide being quantitative. This last reaction can be considered as being composed of the following steps:[14,21]

$$RP^+Ph_3 + OH^- \rightleftarrows RPPh_3OH \qquad (20)$$

$$RPPh_3OH + OH^- \rightleftarrows RPPh_3O^+ + H_2O \qquad (21)$$

$$RPPh_3O^- \rightarrow PPh_3O + R^- \qquad (22)$$

$$R^- + H_2O \rightarrow RH + OH^- \qquad (23)$$

As with Ph_4P^+,[14] reaction 22 is relatively slow in the time scale of polarography and CV. It is even slower here than for Ph_4P^+. Morever, reaction 20 is also slower since even at room temperature the apparent number of electrons below C_0 = 5 mM $l.^{-1}$ is more than one, being close to two at C_0 = 0.1 mM $l.^{-1}$. The effect of raising C_0 is then to accelerate reaction 20 leading to a decrease of the number of electrons. The effect of proton donor addition can be rationalized on the same basis. The differences noted between ACN and DMF in these respects thus reflect the lower reactivity of OH^- in the first solvent than in the second. Indeed, OH^- is more solvated by residual water of the solvent in the first case, the medium being more acidic.

BTP and ATP. The experimental results show that the reduction process is different on the first and second wave, although coulometry indicates the exchange of one electron in both cases.

On the *first wave*, the radical R· disproportionates and dimerizes without further reduction neither at the electrode nor in solution. PPh_3 is thus formed quantitatively with no phosphine oxide. In other words, the one-electron route is completely predominant. This is also in agreement with the absence of effect upon addition of proton donors. The reduction process can therefore be described as

$$(1) + (2) + \alpha(4) + (1 - \alpha)(6)$$

the balance equation being

$$\begin{aligned} RP^+Ph_3 + 1e \rightarrow PPh_3 + \alpha/2R\text{–}R + (1 - \alpha)/2RH \\ + (1 - \alpha)/2R(\text{–}H) \end{aligned}$$

α is about 0.1, i.e., of the same order of magnitude as the ratio of the dimerization and disproportionation rate constants previously determined for the *tert*-butyl radical.[18]

The following mechanism can be proposed for the reaction occurring on the second wave:

$$(1) + (2) + [\beta(4) + (1 - \beta)6] + (1 + \alpha)[(7) + (15) + (18)]$$

By electron transfer at the electrode (7) the radical R· is converted into the carbanion R^- which initiates a two-electron route competing with the one-electron pathway. This implies that the reduction of R· occurs at more negative potentials than the starting phosphonium. This seems impossible if one only considers the intrinsic reductibility of R·, which is most probably larger than that of the phosphonium. The succeeding reactions involving R^- would even shift the reduction potential positively. However, it must be noted that R· is involved in very fast reactions, dimerization and disproportionation, which shift its reduction potential toward negative potentials. On the other hand, the electron-donating character of the methyl and ethyl groups renders the intrinsic reductibility of R· less than with other phosphoniums, e.g., with R = Ph or a linear aliphatic chain.

In the time scale of the controlled potential electrolysis the balance reaction is the sum of the above steps:

$$\begin{aligned} RP^+Ph_3 + 1e + (1 - \alpha)/(2 - \alpha)H_2O \\ \rightarrow \alpha\beta/2(2 - \alpha)R\text{–}R + \alpha(1 - \beta)/2(2 - \alpha)R(\text{–}H) \\ + [2 - \alpha(1 + \beta)]/2(2 - \alpha)RH + (1 - \alpha)/(2 - \alpha)PhH \\ + (1 - \alpha)/(2 - \alpha)RPPh_2O + 1/(2 - \alpha)PPh \end{aligned}$$

Starting from either the yield in PPh_3 (90%) or in benzene (8%) the same value of α (0.9) is approximately found, showing that the formation of alkene occurs essentially through disproportionation of R· and not through Hofmann degradation.

In the time scale of polarography and CV reaction 8 is slow so that the balance equation is now

$$\begin{aligned} &RP^+Ph_3 + (2-\alpha)e + (1-\alpha)H_2O \\ &\quad \rightarrow \alpha\beta/2RR + \alpha(1-\beta)/2R(\text{-}H) \\ &\quad + [2-\alpha(1+\beta)]/2RH + PPh_3 + (1-\alpha)OH^- \end{aligned}$$

which accounts for the existence of a second wave and the absence of a $RPPh_2O$ wave on the polarograms. However, with the above value of α the second wave should be $1/10$ of the first wave, whereas it is actually about half. This can be explained by the influence of initial concentration. Indeed, at low concentrations a smaller value of α is expected since the one-electron route is composed of two second-order reactions whereas reaction 15, which kinetically determines the competition in the two-electron route, is first order.

ETP and MTP. For both cations, the following reaction scheme can be proposed:

$$\begin{aligned} &(1) + \alpha(2) + \beta(4) + (1-\beta)[(7 \text{ or } 9) + (13) + (17) + (19)] \\ &\quad + (1-\alpha)(3) + \gamma(5) + (1-\gamma)[(8 \text{ or } 10) \\ &\quad + (14) + (17) + (19)] \end{aligned}$$

according to the fact that the OH^- cleavage only yields $RPPh_2O$ without any PPh_3O. The disproportionation of the ethyl radical is neglected in comparison with dimerization since it is about seven times slower.[18] The balance equation is then

$$\begin{aligned} &RP^+Ph_3 + 1e + [1-\alpha\beta-(1-\alpha)\gamma]/[2-\alpha\beta \\ &\quad -(1-\alpha)\gamma]H_2O \rightarrow 1/[2-\alpha\beta-(1-\alpha)\gamma]\{\alpha PPh_3 \\ &\quad + (1-\alpha)RPPh_2 + [1-\alpha\beta-(1-\alpha)\gamma]RPPh_2O \\ &\quad + \gamma(1-\alpha)/2Ph\text{-}Ph + \alpha\beta/2R\text{-}R \\ &\quad + \alpha(1-\beta)RH + [\alpha(1-\beta) + 2(1-\gamma)(1-\alpha)]PhH\} \end{aligned}$$

where α is the ratio of R vs. Ph expulsion in the initial radical, β is the ratio of dimerization vs. further reduction for $R^\cdot$, and γ is the same ratio for $Ph^\cdot$. α can be determined from the equation

$$\alpha/(1-\alpha)\text{: } \%\ PPh_3/\%\ RPPh_2$$

For ETP $\alpha = 0.82$ and, from the fact that no diphenyl is found, $\gamma = 0$. However, γ could be in fact larger, leading nevertheless to practically no diphenyl, since the Ph expulsion in initial radical ($1-\alpha = 0.18$) is a minor pathway as compared to the C_2H_5 expulsion. The fact that $\alpha = 0.82$ shows that the ethyl expulsion is quite significantly larger than expected from a statistic distribution between Et and Ph. This can be explained by the fact that the ethyl radical is more stable than the phenyl radical dissociation energy: Ph–H, 112; Et–H, 98 kcal mol^{-1}.[23] In the phosphine oxide formation the orientation of the cleavage is completely in favor of phenyl expulsion which is to be related to the lower basicity of Ph^- as compared to Et^-.[24]

The relative importance of the two-electron route β can be determined independently from the two equations

$$(1-\alpha\beta)/\alpha = \%\ C_2H_5PPh_2O/\%\ PPh_3$$

$$(2-\alpha-\alpha\beta)/\alpha = \%\ PhH/\%\ PPh_3$$

It is found that $\beta = 0.17$ and 0.09, respectively. β is thus on the order of 10% showing that the one-electron route is markedly less important than the two-electron route.

As regards now the mechanism of phosphine oxide formation it has been seen that a significant amount of ylide is formed, being larger in HMPA than in DMF. This indicates that the carbanion, Et^- or Ph^-, is likely to attack the phosphonium cation rather than water, giving rise to the ylide which then decomposes according to

$$\begin{aligned} &C_2H_4{=}PPh_3 + H_2O \rightleftarrows C_2H_5P^+Ph_3 \\ &\qquad\qquad + OH^- \rightarrow C_2H_5PPh_2O + PhH \end{aligned}$$

Indeed, if Et^- were to react preferentially on water, this would imply water to be a stronger acid than the ETP cation; the above equilibrium would then be intrinsically in favor of the right-hand side and further displaced in the same direction by the nucleophilic attack of OH^- on ETP, with not even a transitory formation of the ylide. The ylide formation is therefore most probably the initial step of the two-electron route.

For MTP, α, β, and γ can be determined from the yields in PPh_3, $MePPh_2$, $MePPh_2O$, and PhPh using the following three equations

$$\alpha/(1-\alpha) = \%\ PPh_3/\%\ CH_3PPh_2,$$

$$\gamma(1-\alpha)/2\alpha = \%\ PhPh/\%\ PPh_3$$

$$[1-\alpha\beta-(1-\alpha)\gamma]/\alpha = \%\ CH_3PPh_2O/\%\ PPh_3$$

and thus the following values are found:

	α	β	γ
ACN	0.53	0.26	0.53
DMF	0.42	0.10	0
HMPA	0.56	0.30	0

α is close to 0.5 in the three solvents, which implies that the CH_3–P cleavage is more important than the Ph–P cleavage. The statistical distribution would correspond to $\alpha = 0.25$, in agreement with the order of reported stabilities of $CH_3^\cdot$ (104 kcal[23]) and $Ph^\cdot$ (112 kcal[23]). The cleavage resulting from the reaction with OH^- leads entirely to CH_3PPh_2O in agreement with the stronger basicity of CH_3^- as compared to Ph^-.[25]

Although the two-electron pathway is still predominant, the one-electron route is more important than in the ethyl derivative and involves the phenyl radical owing to the fact that a significant phenyl cleavage now occurs. The formation of ethane is, however, small, 5% at maximum. Its variation with solvent is not therefore very meaningful. The variation of the diphenyl yield with the solvent is clearer: it reaches 8% in ACN and is negligible in DMF and HMPA. Indirect evidence may be derived from this last observation in favor of the initial formation of the ylide rather than attack of the carbanion on water and subsequent reaction of OH^- on the phosphonium. Indeed, Ph^- can be considered as more reactive toward the phosphonium in HMPA and DMF than in ACN which results in less dimerization in the first two solvents. If the carbanion would react directly on water this reaction would be faster in ACN than in DMF or HMPA leading to less dimerization in the first solvent, contrarily to what is experimentally observed. Initial formation of the ylide followed by decomposition by water thus appears as probable, although it cannot be proved directly.

Conclusion

The results of the present work together with those gained in the previous studies of Ph_4P^+ [14] and phosphoniums leading to stable ylides allow the following conclusions to be drawn:

1. In the whole series the initial cation not only plays the role of an electrochemically reducible material but also interferes in the reaction process as an acid. This is the case for phosphoniums giving rise to stable ylides as the phenacyl, benzhydryl, and benzyltriphenylphosphoniums but also with cations where the ylide formation is not possible. There is then competition between abstraction of a β proton (Hofmann degradation) and attack of the phosphorus by OH^- generated from residual water which results in phosphine oxide formation. Ph_4P^+ is a typical example of phosphine oxide formation. When the nature of R allows the Hofmann degradation the

competition is under the dependence of the water content and reactivity in the solvent because they influence simultaneously the reaction of R^- on water leading to OH^-, the reactivity of R^- on the starting phosphonium, and the nucleophilic reactivity of OH^-. The competition depends also upon the initial concentration since the phosphine oxide formation is a first-order process while the Hofmann degradation is second order toward the phosphonium cation.

In the case of the primary aliphatic R groups such as ethyl and methyl the ylide is unstable toward residual water and decomposes into phosphine oxide. It seems, however, that during the electrochemical reduction the preliminary formation of the ylide occurs rather than direct attack of the phosphorus by OH^-.

2. A competition exists between a one-electron pathway involving dimerization and/or disproportionation of $R^·$ and a two-electron pathway leading to ylide formation, Hofmann degradation, and phosphine oxide formation. In this connection two extreme cases are (1) that of cations giving rise to stable ylides where the two-electron reaction is total; (2) that of tertiary aliphatic R groups where the one-electron reaction is quantitative in the potential region of the first wave. An interesting phenomenon is then the existence of two waves in polarography and in controlled potential electrolysis of two potential regions where the reaction products are different although the numbers of electron exchanged are the same.

In the intermediate cases the competition depends upon the nature and water content of the solvent and on initial concentration. A typical example is the cumyl derivative. It is seen in this case that DMF with a high initial concentration provides the optimal conditions for an almost complete predominance of the one-electron route.

3. The orientation of cleavage is generally not the same in reduction and in phosphine oxide formation upon attack of OH^-. Examples are found where reductive cleavage results in complete R expulsion whereas OH^- attack results in complete phenyl expulsion. Orientation of the two cleavages can be related respectively to the stabilities of the various $R^·$ as compared to $Ph^·$ as featured by dissociation energies of RH and to the basicities of R^- as compared to Ph^-.

Experimental Section

Chemicals. The origin and purification of solvents and supporting electrolytes were the same as already described.[13,14]

The phosphonium salts were prepared either by reacting the alkyl bromide with triphenylphosphine[5] (methyl and ethyl derivatives) or starting from the alcohol according to Pommer[26]

$$ROH + PPh_3H^+, ClO_4^- \rightarrow RP^+Ph_3, ClO_4^- + H_2O$$

(for all the other phosphoniums).

Many of the other chemicals were of commercial origin. They were recrystallized or distilled before use. *tert*-butyl-, *tert*-amyl-, methyl-, and ethyldiphenylphosphine oxides and 1,1-diphenylethane were obtained from the reaction of Bu_4NOH on the corresponding phosphoniums; dicumene and 2,2,3,3-tetraphenylbutane from preparative scale electrolysis.

Electrochemical Instrumentation and Procedures. Instrumentation and procedures for polarography and cyclic voltammetry have been described elsewhere[13,14] and also the use of a glove box for the work in HMPA.[13]

Three types of cells were used for controlled potential electrolysis and coulometry.

For concentrations in the millimolar range, the working electrode was a 40-cm^2 mercury pool and the counterelectrode a platinum wire. They were separated by a no. 4 porosity glass frit. The volume of solution was 40–60 cm^3, the maximal currents 50–100 mA, and the electrolysis time about 10 min. The electrolyses are followed by in situ polarography or CV.

In the 5–50 mM $l.^{-1}$ range two types of electrolysis were performed: analytical scale and preparative scale. (1) Analytical scale: the mercury pool surface area was 13 cm^2, the volume of solution 10 cm^3, and the anodic and cathodic compartments were separated by a clay cylinder (Haldenwanger, ABS). The electrolysis durations were on the order of 20 min. (2) Preparative scale: electrodes and diaphragm were the same as above but the cathode surface area was 40 cm^2 and the volume of solution was 250 cm^3. The electrolysis durations were on the order of several hours.

Analysis of the Electrolyzed Solutions. Preparative scale electrolyses were followed by extraction of products from the solvent and supporting electrolyte, using ether, benzene, or cyclohexane. In the analytical scale electrolysis the analysis was performed directly on the solutions without extraction.

Polarography and CV were used for titrating PPh_3O and $RPPh_2O$ by their reduction waves and PPh_3 by its oxidation wave on mercury. Most of the reduction products were analyzed by VPC on SE-30, Carbowax 20M, or OV-17 columns.

Acknowledgment. The work was supported in part by the Centre National de la Recherche Scientifique (Equipe de Recherche Associé no. 309, Electrochimie Organique).

Registry No.—CTP, 61363-41-5; DTP, 61363-42-6; BTP, 47250-88-4; ATP, 47316-65-4; ETP, 39895-79-9; MTP, 15912-74-0.

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