Electrochemical and Electron Paramagnetic Resonance Studies of a Series of Phosphonium and Ammonium Salts. Studies Concerning the Conjugative Interaction of a Tetravalent Phosphorus Atom

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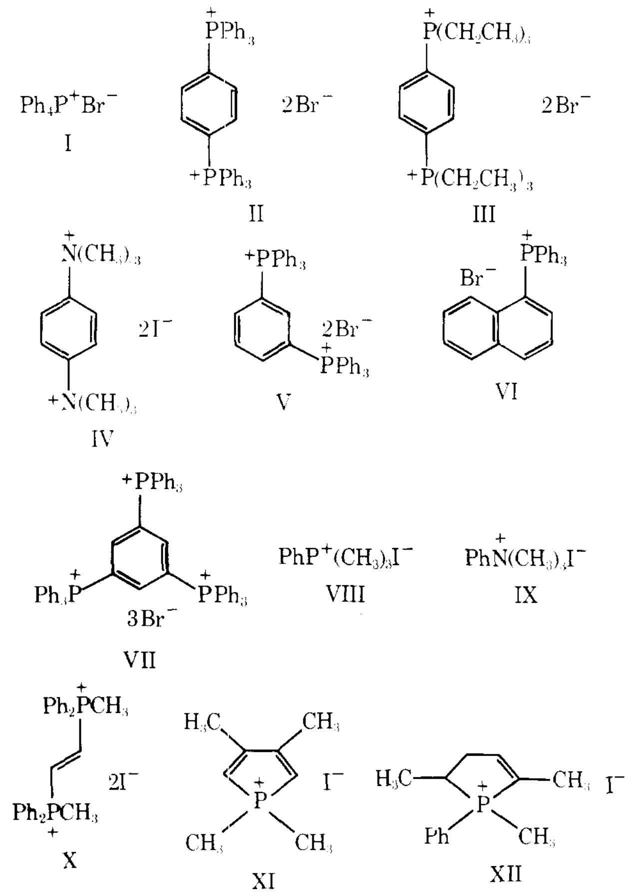
Several ammonium and phosphonium salts were reduced electrochemically in acetonitrile (AN). Four of the phosphonium salts were found to yield stable reduction products at the first wave. Electron paramagnetic resonance spectra are reported for two of these radicals (II and VII). The basis of the stability of the reduction products of phosphonium salts is discussed in terms of conjugative interaction of tetravalent phosphorus atoms.

Until recently, the electrochemistry of phosphonium salts has been predominantly concerned with the synthetically useful reductive cleavage reaction generally carried out in aqueous media.[1] Nonaqueous, aprotic solvents have been utilized in only a few instances, and most of the studies have centered on $Ph_4P^+X^-$.[2-6,15] We reported earlier the unusual observation that the one-electron reduction products of 1,4-diphosphoniacyclohexa-2,5-diene salts and phosphonium-substituted nitrobenzene compounds were quite stable.[7-10] These studies provide strong experimental evidence that a tetravalent phosphorus atom can interact conjugatively with π systems. In this paper, we would like to report additional electrochemical studies on a series of phosphonium and ammonium compounds which provide additional information on the question of conjugative interaction of a tetravalent phosphorus atom. This study also provides additional information on some of the structural features necessary in a phosphonium salt which will yield a relatively stable one-electron reduction product.

Chart I



Results

Electrochemistry. The structures of the compounds studied in this work are given in Chart I. The polarographic and cyclic voltammetric (CV) data for these compounds are presented in Tables I and II.

Compounds II, III, VII, and XI exhibit several reductive waves. The first wave appears to be a reversible one-electron reduction, and the reduction products appear to be very stable. This is demonstrated by the values of i_{pa}/i_{pc} of unity at slow to moderate (<0.5 V/s) sweep rates (Table II). The values of $E_{pa} - E_{pc}$ (Table II) and $E_{3/4} - E_{1/4}$ (Table I) are near the one-electron, reversible charge-transfer value of 56 mV.[11,12] The limiting currents for these compounds are proportional to the square root of the corrected height of the mercury column, and the cathodic peak current (i_{pc}) divided by the square root of the sweep rate is also constant.[12-14] The one-electron nature of the most anodic reduction wave of these compounds was confirmed by the observation of electron paramagnetic resonance (EPR) spectra when salts II, III, and VII were reduced at potentials corresponding to this wave. Furthermore, the diffusion current constants (I_d) of these compounds (Table I) are in the range for one-electron reductions (1–3).[9,10,13]

Compound I has been extensively studied in nonaqueous solvent systems.[2,5,6] At slow sweep rates there is no anodic current in the CV, but at very fast sweep rates (100 V/s) significant anodic current is observed.

As noted above, the electrochemistry of III at the first reduction wave is straightforward (i.e., chemically and electrochemically reversible). There is no difference in this behavior in AN or DMF or at platinium or mercury electrodes. There is a difference of 60 mV in $E_{1/2}$ between DMF and AN (Tables I and II).

Compound IV exhibits several maxima in its polarogram in both DMF and AN. Similar complications are observed at the hanging mercury drop electrode (HMDE). In AN, the reduction at a platinum bead electrode (PBE) is obscured by solvent breakdown. However, in DMF at the PBE uncomplicated reduction waves are observed. No evidence for anodic current from the first wave was observed at 10 V/s and higher sweep rates.

There is a maximum in the polarogram of V on the rising portion of the wave, and the CV has an unusual shape. The $E_{1/2}$ of −1.36 V was estimated from that portion of the wave not obscured by adsorption. E_{pc} is dependent on ν, and there is no anodic current in the CV up to 0.5 V/s.

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Table I. Polarographic Data for Phosphonium and Ammonium Salts[a]

	first wave				second wave		third wave		fourth wave
compd	$-E_{1/2}$, V	i_d, μA	I_d	$E_{3/4} - E_{1/4}$, mV	$-E_{1/2}$	i_d, μA	$-E_{1/2}$, V	i_d, μA	$-E_{1/2}$, V
I	1.868	3.70	2.34	37	2.6^{d}	*d*			
II	1.212	3.20	1.84	51	1.59	1.75	1.87	1.95	2.57^{d}
III	1.490	3.36	2.38	54	~2.2^{e}	2.70			
III^{b}	1.430^{b}	2.15^{b}	1.49^{b}	57^{b}	1.83^{b}	0.4^{b}	2.1^{b,e}	1.75^{b}	
IV	2.05^{e}				2.4^{e}		2.65^{e}		
IV^{b}	2.0^{b,e}				2.3^{b,e}				
V	1.36^{c}	3.15	2.00		1.88	3.1			
VI	1.604	4.5	2.46	37	2.58	15			
VII	0.994	1.65	1.36	54	1.36	1.7	1.7^{c}	2.5	
VIII	1.9^{f}	0.9			2.23^{c,e}	4.9			
IX	2.5^{c,e}	11							
X	0.849	3.7	2.39	39	2.1^{c,e}	2.7			
XI^{g}	1.439	3.77	3.02	54	2.28	3.15			
XII	2.2^{c}	3.6	2.55						

[a] The solvent was acetonitrile (AN) with 0.1 M tetraethylammonium perchlorate (TEAP) as a supporting electrolyte. The reference was the saturated colomel electrode. [b] The solvent was dimethylformamide (DMF) with 0.1 M TEAP as a supporting electrolyte. [c] Maxima complicated the wave. [d] Shoulder on the solvent breakdown current. [e] Peak of maxima. [f] Prepeak. [g] Depression in the limiting current at −1.85V.

Table II. The First Wave of Cyclic Voltammetric Data for Phosphonium and Ammonium Salts[a]

compd	E_{pc}, V	$E_{pa} - E_{pc}$, mV	i_{pa}/i_{pc}	ν, V/s	electrode
I	1.95		0	0.2	Hg
	2.05	110	0.5	100	Hg
II	1.26	65	0.87	0.05	Hg
	1.26	66	1.02	0.20	Hg
III	1.53	65	0.95	0.05	Hg
	1.53	64	1.00	0.10	Hg
	1.53	67	1.03	0.05	Pt
III (DMF)	1.47^{b}	60^{b}	1.01^{b}	0.10	Hg
III (DMF)	1.47^{b}	64^{b}	1.04^{b}	0.05	Pt
IV (DMF)	1.97^{b}		0	0.10	Pt
IV (DMF)	2.23^{b}		0	10	Pt
V	1.38		0	0.05	Hg
	1.44	*c*	*c*	30	Hg
VI	1.67		0	0.2	Hg
	1.70	75 ± 5	small	20	Hg
VII	1.03	60	0.98	0.02	Hg
VIII	2.28		0	0.20	Hg
	2.28	80	0.2	100	Hg
IX	2.35		0	100	Hg
X	0.91		0	0.20	Hg
	0.97	82	0.86	10	Hg
	0.98	85	1.0	63	Hg
XI	1.49	60	0.61	0.05	Hg
	1.49	62	0.88	0.30	Hg
XII	2.14		0	0.20	Hg
	2.14		0	5.0	Hg

[a] AN, 0.1 M TEAP. [b] DMF, 0.1 M TEAP. [c] See text.

In the CV of VI at slow sweep rates there is no anodic current corresponding to the initial reduction wave. At 20 V/s, anodic current from the first reduction wave becomes perceptible.

The CV of compound VIII in AN has one main wave at E_p = −2.28 V (0.2 V/s). There is also a small adsorption wave at E_p = −2.0 V. Even at scan rates up to 100 V/s, little anodic current is observed for the main wave. Polarography shows a small wave at about $E_{1/2}$ = −1.95 V and a wave at −2.22 V which is complicated by a maximum on the rising portion of the wave.

In AN, the reduction of IX produces a single wave. The CV of compound IX shows no anodic current at high ν (100 V/s) and is complicated by adsorption. The polarogram (Table I) exhibits an enormous maximum on the rising portion of the wave. The $E_{1/2}$ was estimated from that portion of the wave discernible after the maximum subsides.

The polarography of the first wave of X (−0.849 V) is complicated by a maximum which occurs at the top of the wave in the form of a plateau about 0.1 V wide and 0.7 μA above the current to which the wave decays. The CV of the first wave of compound X at 0.2 V/s shows no anodic current. However, when the sweep rate is increased to 5 V/s, anodic current is observed.

The CV of XI reveals a peak (E_{pc} = −1.28 V) which is barely perceptible in the polarogram. This peak grows faster than the peak at E_{pc} = −1.49 V as ν is increased. The peak at −1.28 V does not appear when the PBE is used. This behavior indicates that the most positive reduction of XI is a prepeak. When a separate peak is observed for the reduction of an adsorbed species, the presence of adsorption does not shift the main reduction from the reversible value.[16]

The polarography of XII is complicated by an enormous maximum at −2.2 V which decays by −2.3 V to reveal the crest of the wave. On CV at 0.2 V/s there are waves at E_{pc} = −2.14 and −2.25 V; above 0.3 V/s the second of these is not observed. Since adsorption is less important relative to faradic processes at low ν,[16] it seems that the more cathodic process is the uncomplicated reduction of XII, while the reaction at −2.15 V is reduction of XII with the product strongly adsorbed.

With the exception of compounds VIII, IX, and XII, all compounds exhibited limiting polarographic currents which were proportional to the square root of the corrected height of the mercury column.

Electron Paramagnetic Resonance Studies. The one-electron reduction products of II, III, and VII were studied by EPR. An unsuccessful attempt was made to observe the EPR of the one-electron reduction product of XI.[36] The radical cations were generated by reduction at a potential corresponding to the plateau of the first wave for each compound. The hyperfine splitting constants are given in Table III. In the

Table III. Hyperfine Coupling Constants of Reduced II and VII

	hyperfine splitting constant (hfsc)[a]	
compound	a_H, G	a_p, G
II	1.89	11.94
VII	3.50	5.33

[a] 1 gauss = 0.1 mT.

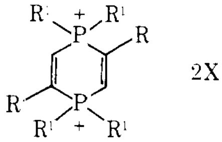
case of VII, the phosphorus coupling constant was assigned the larger value by analogy with several reported radicals.[7,9,10,17,18] In II, the assignments are unequivocal. The EPR of III has been discussed elsewhere.[19]

Also, the assignments are in good agreement with Hückel molecular orbital calculations. The proton coupling constants for $II^{+}\cdot$ (1.89 G) are similar to those for p-dinitrobenzene (1.21 G).[20] No couplings were observed from the "peripheral" phenyl substituents on the phosphorus atoms in either $II^{+}\cdot$ or $VII^{2+}\cdot$.

In addition to correlating the EPR data, the HMO calculations were found to also correlate well with the half-wave reduction potentials.[37]

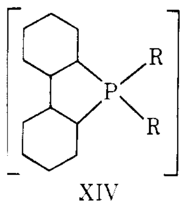
Discussion

There have been very few reports of phosphonium salts which yield relatively stable reduction products.[23] In most cases, the reduced phosphonium salts rupture one or more carbon–phosphorus bonds to yield a phosphine and alkyl or aryl radical. We have recently reported that several 1,4-diphosphoniacyclohexa-2,5-diene salts[8,10] (XIII), as well as some



XIII

ammonium and phosphonium derivatives of nitrobenzene,[9] yield very stable one-electron reduction products. In addition, recently the EPR spectra of biphenyl compounds (XIV) have



XIV

been reported.[21] In this paper, we have reported three other types of phosphonium salts which yield stable reduction products (II, III, VII, and XI). It is clear from the previous reports and from the compounds reported here that the generation of a stable reduced phosphonium salt requires extensive delocalization of the added electron. As in the case of I, IV, VI, VIII, IX, X, and XII, and also in most of the earlier reports, the extra electron is entering an antibonding molecular orbital which has considerable antibonding character between the carbon–phosphorus bond. However, in the case of II, III, and VII, as well as in the diphosphoniacyclohexa-2,5-diene salts and nitrobenzene derivatives, the added electron is extensively delocalized over the whole molecule. In the cases of II, VII, and the diphosphoniacycohexa-2,5-diene salts, the symmetrical location of the tetravalent phosphorus atoms would lead to a small fraction of the added electron being associated with each phosphorus atom.

The remarkable difference in reductive characteristics of III and IV provides additional strong evidence for the conjugative interaction of a tetravalent phosphorus atom with a π system. Compounds III and IV should act very similarly if the phosphonium substituents are acting only in an inductive manner as the ammonium substituents must. However, IV is more difficult to reduce by more than 0.5 V. Also, the rate constant for decomposition of $IV^{+}\cdot$ is at least several orders of magnitude greater than that for $III^{+}\cdot$ (Table II). This difference in behavior cannot be attributed to the difference between ethyl and methyl substituents as this difference, if measurable, would be very small.[22] Whether this conjugative interaction involves 3d, 3p, or higher shell orbitals is not clear; however, these observations cannot be explained in terms of a purely inductive interaction.

Compound $VII^{2+}\cdot$ could have conceivably yielded information on the conjugative interaction of the $-PPh_3^+$ groups by determining the spin densities at all six carbon atoms of the benzene ring. However, we were not able to see the splitting of the natural abundance ^{13}C, and hence the spin densities at the three carbon atoms to which the $-PPh_3^+$ groups are attached are unknown. The dication radical is capable of undergoing Jahn–Teller distortions and could show up as very broad lines in the EPR. The relatively sharp lines do not suggest that this process is going on.

Compounds XI and XII also show considerable difference in reductive characteristics. Compound XI yields a substantially more stable reduction product than XII. Unfortunately $XI\cdot$ was not stable enough to determine its EPR. This would have indicated if considerable spin density was on the phosphorus atom. However, the results are consistent with the conjugative interaction of the tetravalent phosphorus atom either in a cyclic through conjugation fashion or in the Dewar "Island Model".

In conclusion, three new types of phosphonium salts which yield relatively stable reduction products are reported. The requirements of phosphonium salts which are necessary to yield stable reduction salts are discussed. These factors will be of interest to the biological studies on many of these phosphonium salts. Finally, strong experimental evidence is presented which supports the concept that tetravalent phosphorus atoms can interact conjugatively with π systems.

Experimental Section

Melting points were taken with a Thomas-Hoover oil bath melting point apparatus and were corrected. Infrared spectra were obtained with a Perkin-Elmer 257 spectrometer. A Hewlett-Packard Model S750-B gas chromatograph was used. NMR spectra were recorded on a JEOL C-60HL spectrometer. EPR spectra were determined on a JEOL JES-ME-3x instrument. Temperatures were determined with a copper–constantan thermocouple. Computer simulations of theoretical EPR spectra were done using a Fortran IV program for mixtures employing Lorentzian line shapes written by R. G. Griffin.[24] The program used for the Hückel MO calculations was written by Munch and Rieke[25] and modified by T. H. Ridgeway for simplified input. Elemental analyses were obtained from Galbraith Laboratories (Knoxville, Tenn.). UV spectra were taken on a Unicam SP 800B spectrophotometer. Most of the electrochemical studies were performed on a UNC Electrochemistry unit designed and built by Fox.[26] A Data Technology Model 351 digital voltmeter was used to accurately determine initial potential settings.

Data were recorded on a Hewlett-Packard Model 7004-B X-Y recorder, a Tektronix type R564B oscilloscope with two type 2A63 modules, and a Tektronix C-12 polaroid camera unit or a Houston Omnigraphic X-Y recorder. All salts were dried in vacuo at 100 °C before use.

Tetraphenylphosphonium Bromide. Compound I was purchased from Columbia Organic Chemicals, mp 283–284 °C (lit. mp 337[27] and 265–267 °C[28]).

p-Phenylenebis(triphenylphosphonium) Dibromide (II). Compound II was prepared by the method of Horner.[28] p-Dibromobenzene (2.36 g, 10 mmol; Aldrich), Ph_3P (10.5 g, 40 mmol; Aldrich), and anhydrous $NiBr_2$ (4.4 g, 20 mmol; Alfa) were loaded into a beaker and placed in a stainless steel bomb which was sealed. This process was carried out in a drybox under N_2. The bomb was placed in an oven at 205 °C for 2.5 h. After cooling, the dark green solid in the beaker was heated in about 200 mL of water at 90 °C. The aqueous solution was cooled and extracted twice with ether and then with CH_2Cl_2. The CH_2Cl_2 solution was dried with sodium sulfate and the solvent stripped off, leaving an oil which was dissolved in water, filtered through Norit, and cooled. White crystals resulted, mp > 360 °C (lit. mp 286[28] and 300 °C[29]). Molecular weight calculated for $C_{42}H_{34}P_2Br_2$: 760. Found: 740.

m-Phenylenebis(triphenylphosphonium) Dibromide (V). Compound V was prepared by the method outlined for II, mp 348 °C. Anal. ($C_{42}H_{34}P_2Br_2$) P, Br.

α-Naphthyltriphenylphosphonium Bromide (VI). Compound

VI was prepared by the method outlined for II (molar ratios adjusted to give an excess of aryl halide[28]), mp 240–243 °C (lit.[28] mp 243 °C).

1,3,5-Tris(triphenylphosphonium)phenyl Tribromide (VII). Compound VII was prepared by the method outlined for II with adjusted molar ratios of reagents, mp 293–295 °C (lit.[28] mp 295–297 °C).

Phenyltrimethylphosphonium Iodide (VIII). Bromobenzene (10.2 g, 0.066 mol) and trimethylphosphine (2.5 g, 0.033 mol; Pfaltz and Bauer) were combined in a beaker and placed in a stainless steel bomb. The bomb was heated at 110 °C for 10 days and then at 200 °C for 1 day. After cooling, the solid was triturated with ether and crystallizated from water. The yield of VIII as the bromide was 3.67 g (47%), mp 275 °C. Aqueous NaI was added to an aqueous solution of VIII (Br^-). The resulting precipitate of iodide recrystallized from water, mp 228.5–230 °C (lit.[30] mp 236 and 205 °C).

Phenyltrimethylammonium Iodide (IX). Compound IX was prepared by adding *N,N*-dimethylaniline to excess methyl iodide, heating on a steam bath momentarily, and filtering. It was recrystallized from water, mp 225–228 °C (lit.[31] mp 228 °C).

***trans*-Ethene-1,2-bis(methyldiphenylphosphonium) Diiodide (X).** Compound X was prepared by the method of Brophy and Gallagher.[32] *trans*-Ethene-1,2-bis(diphenylphosphine) (Pressure Chemical Co.; 1 g, 2.54 mmol) was treated with excess CH_3I at ambient temperature for 30 min. The liquid was decanted, leaving an oil clinging to the walls of the flask. Methyl alcohol was added with heating, causing immediate crystallization of the oil to bright yellow platelets: yield 1.34 g (78%); mp 280 °C (lit.[32] mp 242–245 °C).

1,1,3,4-Tetramethylphospholium Iodide (XI). Compound XI[33] was a gift from L. D. Quinn, Duke University.

1-Phenyl-1,2,5-Trimethyl-2-Phospholenium Iodide (XII). Compound XII[34] was a gift from L. D. Quinn, Duke University. The sample was a mixture of the *cis*-dimethyl and *trans*-dimethyl isomers.

Electrochemistry. Two methods were used for the preparation of dry acetonitrile. CH_3CN (Fisher commercial) was rapidly distilled from $KMnO_4/Na_2CO_3$ and stored over dry 4Å molecular sieves (24 h at 200 °C in vacuo) (MCB). Alternatively, spectrograde acetonitrile (MCB) was treated with dry molecular sieves. The water content from either of these procedures was 1 mM or less.

Dimethylformamide was prepared by allowing spectrograde DMF (MCB) to stand over dried 4Å molecular sieves overnight followed by vacuum distillation (≤ 1 mmHg) with ice water circulated through the condenser. The DMF was stored under N_2 at room temperature.

Tetraethylammonium perchlorate (TEAP) was prepared by dissolving tetraethylammonium bromide in boiling water and adding perchloric acid. The TEAP was filtered and recrystallized twice from distilled water and dried at 60 °C in vacuo. It was again dried immediately before each use.

Water analyses were done using the method of Hogan et al.[35] Analyses were done using a 6 ft column of Porpak Q, 80–100 mesh (Waters Associates). Injection volumes were 50 μL.

Water content of the solution in the cell was determined by withdrawal of a 50-μL sample directly from the cell and injecting it in the GC. The water content was determined by comparison of the area of the peak to that of a standard. Water concentration in the cell was found to be 5–10 mM, and determinations were considered accurate ±1 mM.

Bethlehem instrument grade mercury was used in the precision hanging mercury drop electrode (Metrohm); triple distilled mercury was used for polarography.

The platinum bead electrode (PBE) was cleaned with aqua regia before each use.

The dropping mercury electrode (DME) used was characterized by $m^{2/3}t^{1/6} = 1.40$ and $m = 1.04$ mg/s at 40 cmHg; at 50 cmHg, $m^{2/3}t^{1/6} = 1.57$ and $m = 1.28$ mg/s; at 60 cmHg, $m^{2/3}t^{1/6} = 1.64$ and $m = 1.41$ mg/s.

The cell and general procedure have been described previously.

Nitrogen was passed through a dry ice/acetone trap, Drierite, dried molecular sieves, and a saturator containing the proper dry solvent. This nitrogen was used to degass the electrochemical solutions. Once degassing was complete, the N_2 stream was diverted over the solution surface.

The cell for in situ generation of radicals in the EPR spectrometer has been previously described.

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Registry No.—I, 2751-90-8; II, 10111-14-5; III, 63216-62-6; IV, 5369-38-0; V, 67745-94-2; VI, 10111-22-5; VII, 10111-29-2; VIII, 1005-21-6; IX, 98-04-4; X, 13466-74-5; XI, 37737-13-6; *cis*-1-phenyl-1,2,5-trimethyl-2-phospholenium iodide, 67745-95-3; *trans*-1-phenyl-1,2,5-trimethyl-2-phospholenium iodide, 67745-96-4; triphenylphosphine, 603-35-0; bromobenzene, 108-86-1; trimethylphosphine, 594-09-2; *trans*-ethene-1,2-bis(diphenylphosphine), 983-81-3; methyl iodide, 74-88-4; *p*-dibromobezene, 106-37-6.

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