(1969).
(4) F. G. Bodewig and J. A. Plambeck, *J. Electrochem. Soc.*, **117**, 904 (1970).
(5) D. M. Gruen, R. L. McBeth, and A. J. Zielen, *J. Am. Chem. Soc.*, **93**, 6691 (1971).
(6) C. H. Liu, A. J. Zielen, and D. M. Gruen, *J. Electrochem. Soc.*, **120**, 67 (1973).
(7) P. Cescon, F. Pucciarelli, V. Bartocci, and R. Marassi, *Talanta*, **21(7)**, 783 (1974).
(8) R. Marassi, G. Mamantov, and J. Q. Chambers, *Inorg. Nucl. Chem. Lett.*, **11**, 245 (1975).
(9) L. Redey, I. Porubszky, and I. Molner, International Power Sources Symposium Committee, International Power Sources Symposium, 9th Brighton, Sussex, England, September 17-19, 1974.
(10) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, **120**, 223 (1973).
(11) G. Lauer, H. Schlein, and R. A. Osteryoung, *Anal. Chem.*, **35**, 1789 (1963).
(12) L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.*, **121**, 212 (1974).
(13) D. E. Bartak and R. A. Osteryoung, *J. Electrochem. Soc.*, **122**, 600 (1975).
(14) K. A. Paulsen and R. A. Osteryoung, 170th National Meeting of the American Chemical Society, Chicago, Ill., 1975.
(15) R. H. Abel, J. H. Christie, L. L. Jackson, J. G. Osteryoung, and R. A. Osteryoung, to be published.
(16) P. L. King and B. J. Welch, *Proc. Australas. Inst. Min. Metall.*, **246**, 7-12, (1975).
(17) B. Cleaver, A. J. Davies, and D. H. Schiffrin, *Electrochim. Acta*, **18**, 747-760 (1973).
(18) W. Giggenbach, *Inogr. Chem.*, **10**, 1308 (1971).
(19) J.-P. Bernard, A. de Haan, and H. Van der Poorten, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **278**, 587 (1973).
(20) B. Meyer, "Elemental Sulfur, Chemistry and Physics", Interscience, New York, N.Y., 1965.
(21) R. Naumann and Ch. Weber, *Z. Anal. Chem.*, **253**, 111-113 (1971).
(22) P. Hagenmuller, J. Rouxel, J. David, A. Colin, and B. LeNeidr, *Z. Anorg. Allg. Chem.*, **323**, 1 (1963).

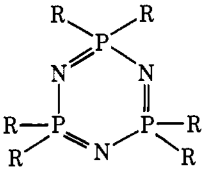
Electrochemical and Electron Paramagnetic Resonance Studies of a Series of Ammonium and Phosphonium Compounds

Reuben D. Rieke,*[1] C. Kenneth White, and Charles M. Milliren

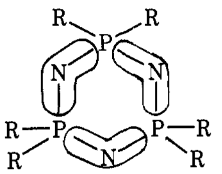
Contribution from the William Rand Kenan, Jr., Laboratories of Chemistry, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received July 28, 1975*

Abstract: Electrochemical studies were conducted on a variety of ammonium and phosphonium derivatives of nitrobenzene. The stable one-electron reduction products were also studied by electron paramagnetic resonance. Hückel as well as CNDO molecular orbital calculations were carried out on these molecules. Evidence for significant conjugative interaction of the phosphonium substituents is presented. Finally, several phosphonium and ammonium compounds were prepared which gave stable one-electron reduction products.

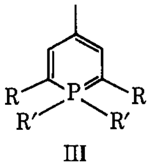
The significance of conjugative interaction involving tetravalent phosphorus has been the subject of a large number of investigations over the past 15 years and the problem is still not clearly resolved.[2] Most of the work has been directed toward the phosphazenes (I), which have at various times been proposed to be stabilized by dπ-pπ bonding in a cyclic manner[3] or an "island" manner[4] (II) or by no dπ-pπ bonding at all.[5,6] Other systems that have received attention are the phosphorines (III) and ylides (IV). Theories similar to those mentioned above have also been proposed in these cases,[7-15] but there appears to be no unequivocal proof of any of the models of dπ-pπ bonding.[2,6,11,12]



I



II



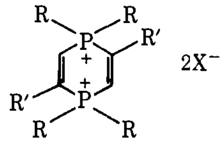
III

$R_3P{=}CR'R''$

IV

The present work extends the study of phosphorus conjugative interaction to phosphonium salts by application of electrochemistry (EC), electron paramagnetic resonance (EPR) and molecular orbital (MO) calculations.

In general the initial reduction products of phosphonium salts are unstable,[18-25] but it has recently been demonstrated that radical cations produced by the reduction of diphosphonium salts (V) are very stable.[16,17] Stabilization of the radical cation by d-orbital participation was proposed.[16] The present work describes new stable radicals from reduction of phosphonium and ammonium salts.



V

Results

Electrochemistry. Five onium derivatives of nitrobenzene (4-nitrophenyltriphenylphosphonium iodide (VI), 3-nitrophenyltriphenylphosphonium iodide (VII), 4-nitrophenyltrimethylammonium chloride (VIII), 3-nitrophenyltrimethylammonium chloride (IX), and 3-nitrophenyltrimethylammonium iodide (X)) were studied by dc polarography and cyclic voltammetry (CV) in acetonitrile (AN).

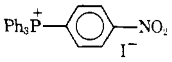
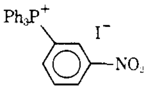
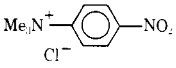
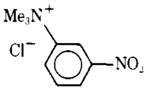
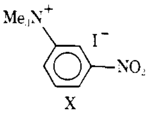
In each case, these nitrobenzenes were observed to have their first reduction wave positive of −1.0 V. Polarographic results for VI-X are given in Table I. Table II gives CV data at 50 mV/s for the first wave of these compounds. The value of unity for i_{pa}/i_{pc} indicates that the reduction product is stable.[26] The

Table I[c]

Compd	$-E_{1/2}{}^1$	$i_d{}^1$	$-E_{1/2}{}^2$	$i_d{}^2$	$-E_{1/2}{}^3$	$i_d{}^3$	$-E_{1/2}{}^4$	$i_d{}^4$	$-E_{1/2}{}^5$	$i_d{}^5$	$-E_{1/2}{}^6$	$i_d{}^6$
VI	0.759	3.40	~1.4[a]	13.20	2.5	3.1						
VII	0,864	3.35	1.39	2.5	1.61	3.0	1,79	5.1	2.55	3.5		
VIII	0.890	3.18	1.42	3.61	1.9	2.95						
IX	0.880	2.90	1.55	3.0	1.82	1,85	2.00	1.30	2.33	0.58	2.55	2.70
X	0.892	1.62	1.38	6.65	2.55[b]	~3.7	2.65	3.5				

[a] Wave extends from −1.1 to −1.7 V, with a maximum at −1.4 V. [b] Position of maximum peak. [c] $E_{1/2}$ values are ±10 mV.

Table II. Cyclic Voltammetry of Derivatives of Nitrobenzene at 50 mV/s

Compound	$-E_{pc}$	$-E_{1/2}{}'^{a}$	$E_{pa} - E_{pc}$	i_{pa}/i_{pc}	Electrode
 VI	0.79	0.76	60	0.98	Hg
	0.79	0.76	63	0.93	Pt
 VII	0,92	0.88	62	0.99	Hg
	0.95	0.93	55	0,95	Pt
 VIII	0,94	0.91	60	0.99	Hg
	0.94	0.91	70	0.96	Pt
 IX	0.93	0.90	62	0,98	Hg
	0,93	0.90	62	0.95	Pt
 X	0.94	0.91	64	1.03	Hg
	0.95	0.93	55	0,95	Pt

[a] $E_{1/2}{}' = E$ at $i = 0.85 i_{pc}$.

Table III. Polarographic Data for the First Reduction Wave of Derivatives of Nitrobenzene

Compd	$-E_{1/2}{}^a$	$E_{3/4} - E_{1/4}$, mV	$I_d{}^d$
VI	0.759	56	2.63
VIa[b]	0.745	56	
VII	0,864	57	2.50
VIII	0,890	60	2.53
IX	0.880	55	2.53
X	0.892	56	
Xa[c]	0.913	56	3.34

[a] ±10 mV. [b] VIa = VI with ClO_4^- as anion. [c] Xa = X with ClO_4^- as anion. [d] The polarographic constant (I_d) is defined as $I_d = i_d m^{-2/3} \cdot t_d{}^{-1/6} C^{-1}$, where i_d is the undamped diffusion current, m is the flow rate of mercury, d is the drop time, and C is the concentration of electroactive substance in the solution.

values of $E_{pa} - E_{pc}$ are near the reversible one-electron value of 56 mV.[27,28] Table II shows little dependence of the electrochemistry of the derivatives of nitrobenzene on electrode material. Neither E_{pc} nor $i_{pc}/\nu^{1/2}$ (ν is the sweep rate) are dependent on sweep rate.

Polarographic data for the first wave of compounds VI–X is presented in Table III. Values of $E_{3/4} - E_{1/4}$ are near the one-electron value of 56 mV.[29] These results are for solutions about 10^{-3} M onium compound. Using pulse polarography the observed $E_{1/2}$ for VIII was −0.917 V at 10^{-4} M and −0.907 V at 10^{-5} M. Sampled dc polarography[30] on compound IX gives $E_{1/2} = -0.910$ at 2×10^{-4} M and $E_{1/2} = -0.891$ at 5×10^{-5} M. Electrocapillary data for 1 mM VII in AN with 0.1 M TEAP shows shortening of the drop life positive of −0.6 V, but no effect at more cathodic potentials. Under the same conditions IX increases the drop life slightly at potentials positive of −0.8 V, but no effect is observed more negatively.

The above data indicate the radical produced by the reduction of onium salts VI–X is stable ($i_{pa}/i_{pc} = 1$). This was confirmed by the observation of EPR signals when some of these compounds were reduced at the potential of their first wave (vide infra). The reversibility of the electrode process is indicated by the values of $E_{pa} - E_{pc}$ and $E_{3/4} - E_{1/4}$. This interpretation of these data require the reaction to be a one-electron transfer. The observation by EPR of radicals produced by reduction at the most anodic wave of some of these onium salts is very strong evidence for a one-electron transfer. The value of the diffusion current constant (I_d) is also indicative of a one-electron process. In acetonitrile, a one-electron reduction of derivatives of nitrobenzene corresponds to I_d = 3–4,[31] meaning that a two-electron reduction would have an I_d of 6–8. The fact that most I_d values on Table III are less than three may be the result of a low diffusion constant for the molecules, possibly related to their charge. The unimportance of complicating factors in the electrode mechanism is indicated by the independence of the cathodic current function of sweep rate, the proportionality of the limiting current to the square root of the mercury column height, the similarity of the reductions on mercury and platinum, the lack of strong dependence of $E_{1/2}$ on concentration, and lack of effect of onium salts on electrocapillary curves in the vicinity of the $E_{1/2}$.

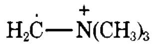
For an uncomplicated, reversible electrode reaction producing a stable product $E_{1/2}$ is approximately equal to $E°$.[27] Therefore, the $E_{1/2}$ values for compounds VI–X have thermodynamic significance and are related to the relative energies necessary to add an electron to the respective compounds.

Comparison of the compounds in Table III that differ only by anion (VI and VIa; IX, X, Xa), reveals that differences in $E_{1/2}$ can result from changes in anion. However, the difference in $E_{1/2}$ due to changing from Cl^- to I^- (IX vs. X) is within experimental error, suggesting that counterion effects on comparisons of phosphonium and ammonium derivatives of nitrobenzene may be neglected.

Electron Paramagnetic Resonance. When compounds VI, VII, VIII, and X are reduced at potentials corresponding to the first reduction wave, EPR signals can be observed. These spectra are reproduced in Figures 1–4 and the hyperfine splitting constants (hfsc) are given in Table IV. A small impurity signal is apparent in Figure 2, undoubtedly causing some perturbation of the spectrum. In spite of this complication, the calculated spectrum closely resembles the experimental spectrum.

The spectrum of VIII was severely broadened, and could only be observed at very dilute concentrations. Due to the high modulation width (4 G) employed in recording the spectra (Figure 4), small splittings may be obscured.

The assignments of hfsc in Table IV were accomplished as follows. In all cases, the triplet caused by splitting from one atom of spin unity was assigned to the nitro nitrogen. This is justified in VIII· and X· by the observation that the nitrogen coupling in XI is only 3.7 G.[12] The odd electron density on the


$\dot{H_2C}-\overset{+}{N}(CH_3)_3$

XI

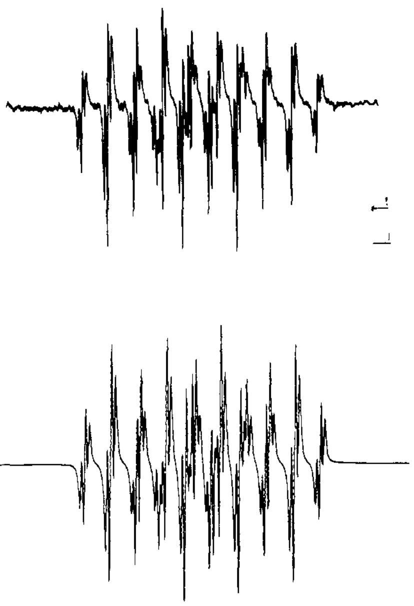


Figure 1. Top: EPR spectrum of VI· generated by electrochemical reduction in AN with 0.1 M TEAP at 0 °C. Bottom: computer simulation using values of hfsc given in Table IV and a line width of 0.2 G.

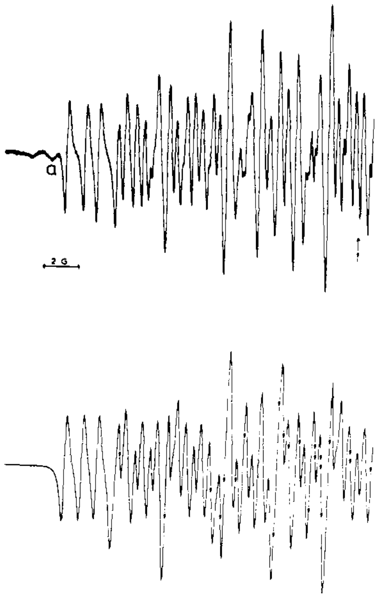


Figure 2. Top: low field half of the EPR spectrum of VII· generated by electrochemical reduction in AN with 0.1 M TEAP at −32 °C. The arrow marks the center of the spectrum. The letter a denotes an absorption line from an impurity. Bottom: computer simulation using the values of hfsc given in Table IV and a line width of 0.2 G.

carbon atoms adjacent to ammonium nitrogens in VIII· and X· must be much smaller than that in XI, indicating that a_N(ammonium) will also be smaller. The 4-G triplet in VIII· is also assumed not to result from the ammonium nitrogen coupling due to the large magnitude and also due to the fact that the triplet has an apparent intensity ratio of 1:2:1 (Figure 4).

The assignment of the phosphorus coupling in VI· is unequivocal, since it is the only single atom of spin one-half (the protons are paired).

The phosphorus atom in VII· is assigned the largest coupling of spin one-half by analogy to VI· and other phosphorus-containing radicals.[17,32]

The various proton hfsc were assigned by analogy to the nitro compounds shown in Table V.

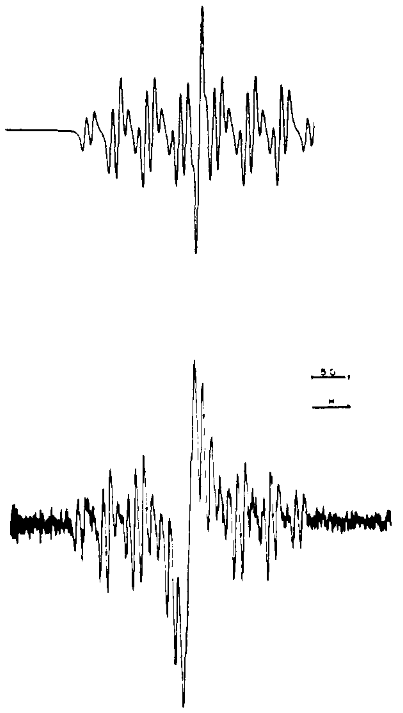


Figure 3. Top: computer simulation of the EPR spectrum of X· using the values of hfsc given in Table IV and 13% uncoupled electron. The line width is 0.4 G. Bottom: EPR of spectrum of X radical generated by electrochemical reduction in AN with 0.1 M TEAP at −19 °C.

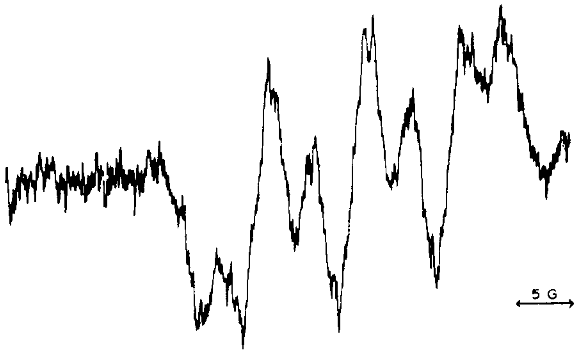


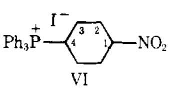
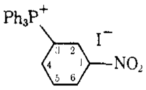
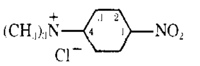
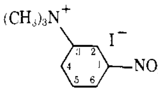
Figure 4. EPR spectrum of VIII· generated by electrochemical reduction in AN with 0.1 M TEAP at 0 °C. The concentration of the radical was very low. The microwave power was 2.0 mV and the modulation width was 4.0 G.

This assignment of proton coupling constants is at variance with HMO calculations (Table VI, vide infra)[33] and should be considered cautiously. It should be pointed out that the assignment of the proton coupling constants are not critical to the arguments presented below. No indications were observed of coupling from "peripheral" substituents on phosphorus.

CNDO Calculations. Complete neglect of differential overlap (CNDO) calculations[42,43] were performed using input data based on recorded bond distances and bond angles for the 1,4-diphosphoniacyclohexa-2,5-diene ring system.[44-46] Atomic coordinates were generated using QCPE 136-COORD[47] and the molecular calculations were performed using QCPE 141 (CNDO/2 and INDO)-CNINDO.[47]

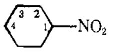
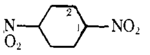
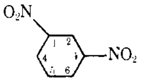
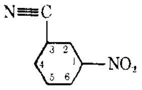
The calculations were performed to determine the predicted contribution of the phosphorus atom to the MO of interest, i.e., either the cationic ground state or the neutral radical. Of particular interest were the mode of contribution of the phosphorus atom to the MO (σ or π) and the type of overlap with adjacent carbons (positive or negative) which might be correlated with the observed physical properties of these systems.

Table IV. Observed Hyperfine Coupling Constants of Radicals from Derivatives of Nitrobenzene

Compd reduced	Atom	Hfsc, G[a]
 VI	2	2,85 ± 0.02
	3	0.42 ± 0.02
	N	6.08 ± 0.02
	P	8.38 ± 0.02
 VII	2	1.7 ± 0.1
	4	2,8 ± 0.1
	5	0.9 ± 0.1
	6	3.2 ± 0.1
	N	8.8 ± 0.1
	P	5.5 ± 0.1
 VIII	2	4
	3	
	N	8.7 ± 0.2
	N (ammonium)	
 X	2	3.4 ± 0.1
	4	3.4 ± 0.1
	5	1.0 ± 0.1
	6	4.4 ± 0.1
	N	8.7 ± 0.1
	N (ammonium)	

[a] 1 G = 0,1 mT.

Table V.[a] Hyperfine Coupling Constants of Radicals from Derivatives of Nitrobenzene

	Atom number, hfsc (G)					
Compd	2	3	4	5	6	N (nitro)
	3.39	1,09	3.97			10,32
	1.12					1.74
	3.11		4.19	1.0	4.19	4,68
	3.18[b]		3.58[b]	0.99[b]	4.54[b]	8.17[b]

[a] Data from ref 34, acetonitrile solvent. [b] Dimethylformamide solvent.

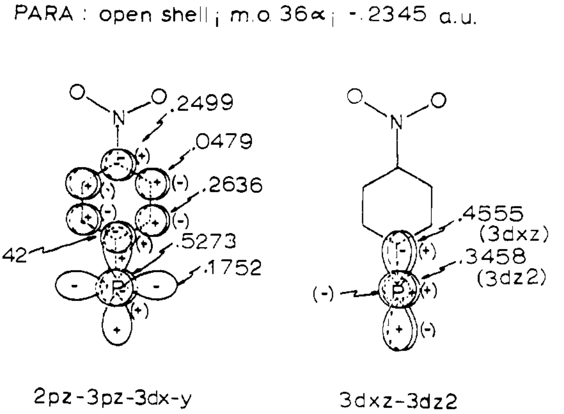


Figure 5.

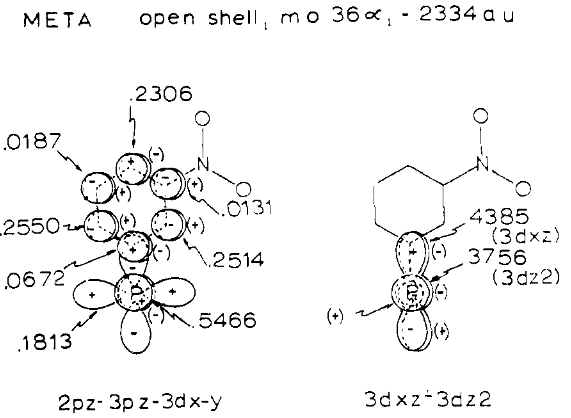


Figure 6.

CNDO calculations were performed on 4-nitrophenyltrimethylphosphonium salt (para) and 3-nitrophenyltrimethylphosphonium (meta) salt. The results are shown pictorally in Figures 5 and 6.

Discussion

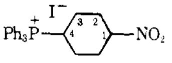
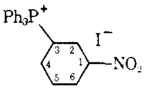
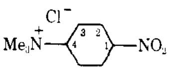
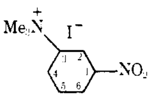
The question of whether 3d orbitals can interact conjugatively and to what extent has been the subject of vast numbers of papers.[2-17] In many cases as much evidence against interaction can be presented as evidence for interaction. It should also be pointed out that in many cases opposing views on the subject center on different molecules. One thing seems clear from the data in the literature, theoretical calculations, and our studies and that is that the conjugative interaction of 3d or 3p orbitals or higher shell levels is dependent on the particular molecule in question and no blanket statement regarding conjugative interaction can be made. Other than the obvious requirement of the correct symmetry, orbital interaction is highly dependent on energy differences of the two orbitals involved and also on the overlap. Calculations on 3d orbitals indicate a very diffuse nature, which should lead to poor overlap.[48] However, calculations have shown that 3d orbitals, in contrast to 2p and 2s orbitals, show a marked contraction as formal charge is introduced on the atom in question.[48] Also an increase in the formal charge is expected to lower its energy. Thus systems with high positive charge associated with the phosphorus atoms should be best suited to show some sort of conjugative interaction.

We feel the experimental data presented in this paper presents strong suggestive evidence for some kind of conjugative interaction of the phosphonium substituents. We do not feel we can define this interaction as being particular to 3d orbitals, 3p orbitals or any other specific orbitals. The results are simply not explainable in terms of inductive effects alone and hence we must invoke a conjugative interaction of some kind.

The highly reversible reduction of compounds VI–X allows one to place some thermodynamic significance on the $E_{1/2}$ values.[27] The fact that compounds VIII, IX, and X have essentially identical reduction potentials, while compound VI has a much lower (105 mV) reduction potential than VII is hard to rationize in terms of a purely inductive model. The ammonium substituents can be assumed to be acting in a purely inductive fashion. The difference between VI and VII can be explained in terms of the classical resonance effects of the para substituent interacting more strongly than the meta substituent. One might take the view that phosphorus being more polarizable might have a greater stabilizing effect in the para position where greater negative charge density is sure to exist. However, one is then faced with the EPR results. The hfsc of the nitro nitrogen in the radicals of VII·, VIII·, and X· are identical within experimental error (8.7 G). On the other hand, the nitro nitrogen of VI· has a much smaller value of 6.08 G. Also, the phosphorus hfsc in VI· is 8.38 G, while for VII· it is only 5.51 G. These results strongly suggest that the phosphonium group is interacting in a conjugative manner and when it is para to the nitro group this interaction is strongest.

While the molecular orbital calculations, either the Huckel

Table VI. Huckel Calculations of Hyperfine Coupling Constants

Compd	Position	Inductive model c^2	Inductive model a_{calcd}[a]	Inductive model Q_p[b]	Conjugative model c^2	Conjugative model a_{calcd}[a]	Conjugative model Q_p[b]	Obsd, G
 VI	2	0.0605	1.43		0.0568	1.17		0.242
	3	0.0817	1.94		0.0630	1.72		2,85
	P	0.1963[c]		42.67	0.1890		44.2	8.38
	N	0.1275	2.56		0.1190	2.0		6.07
	O	0.1406			0.1270			
 VII	2	0.0643	1.52		0.0597	1.73		1.62
	4	0.1121	2.65		0,1905	4.52		2.63
	5	0.4178	0,99		0,0178	0.42		0,91
	6	0.1534	3.64		0.1568	3.72		3.03
	P	0.0100[c]		551	0.0658		83.5	5,51
	N	0.1777	4.98		0.1560	4.74		8,79
	O	0.1769			0.1501			
 VIII	2	0.0819	1.94					4
	3	0.0416	0.986					
	N(+)	0.1724						
	N	0.1682	4.78					8.7
	O	0.1657						
 X	2	0.0876	2.08					3.4
	4	0.1387	3.29					4.4
	5	0.0295	0.70					1.0
	6	0.1014	2.40					3.4
	N(+)	0.0057						
	N	0.1940	6.05					8.7
	O	0.1844						

[a] Calculated from $a = Q_\rho$ where $\rho = c^2$ and $Q_H = 23.7$, $Q_{CH_3} = 27.2$ and for the nitro group, $a_N = 99.0\ \rho_N - 71.6\ \rho_0$. [b] $Q_\rho = a_\rho / c^2$ where a_ρ is the observed hyperfine coupling of phosphorus. [c] For the inductive model, c^2 is the sum of c^2 for the carbon atoms adjacent to phosphorus.

or CNDO, do not prove or disprove the involvement of 3d, 3p, or higher shell orbitals, it is reassuring to find that they are consistent with the experimental results. The CNDO calculations do show strong involvement of 3d and 3p orbitals in the LUMO for the phosphonium compounds. As CNDO calculations are semiempirical by nature, they, of course, do not prove the existence or involvement of d orbitals. However, in a rather large number of calculations including ab initio calculations on phosphorus containing compounds the inclusion of d orbitals has led to much improved results.[14,49]

In conclusion, strong experimental evidence is presented which supports the conjugative interaction of phosphonium substituents with π systems. This interaction is probably not strong and the overall influence of the phosphonium group will be a combination of inductive and conjugated interactions. Finally, several phosphonium and ammonium compounds which give stable one-electron reduction products were reported.

Experimental Section

General. 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 750-B gas chromatograph was used. NMR spectra were recorded on a JEOL C-60HL spectrometer. EPR spectra were determined on a JEOL JESME instrument. Temperatures were determined with a copper constantan thermocouple. Computer simulation of theoretical EPR spectra was done using a Fortran IV program for mixtures employing Lorentzian line shapes written by R. G. Griffin.[35] 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 the UNC electrochemistry unit designed and built by Fox.[36] A Data Technology Model 351 digital voltmeter was used to accurately determine initial potential settings. The sampled dc, pulse, and differential pulse polarograms were performed using a PAR 174.

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.

***p*-Nitrophenyltriphenylphosphonium Iodide and Perchlorate (VI and VIa).** Compound VI was prepared by the method of Horner.[37] *p*-Nitroaniline (2.8 g, 0.02 mol) and the molar equivalent of sodium nitrite were dissolved in 10 ml of concentrated hydrochloric acid and 10 ml of water at 0 °C. Water (20 ml), in which was dissolved sodium acetate (5.6 g), was added. Triphenylphosphine (5.6 g) dissolved in ethyl acetate (80 ml) was added dropwise with stirring. The resulting solution was acidified, the water layer separated from the ethyl acetate, and the aqueous portion extracted twice with ether. The ethyl acetate solution was extracted twice with water, the extracts being combined with the other aqueous fraction. Addition of an aqueous solution of sodium iodide precipitated the iodide VI, mp 228.5 °C dec (lit.[37] 228 °C). Addition of concentrated perchloric acid to the aqueous solution precipitated the perchlorate VIa, which gave one spot with thin layer chromatography (TLC) on silica gel.

***m*-Nitrophenyltriphenylphosphonium Iodide (VII).** Compound VII was prepared analogously to VI, mp 208-209 °C (lit.[37] 215 °C). Anal. Calcd for $C_{24}H_{19}NO_2PI$: C, 56.39; H, 3.75. Found: C, 56.23, H, 3.78.

***p*-Nitrophenyltrimethylammoium Chloride (VIII).** Compound VIII was prepared by the method of Zaki and Fahim.[38] Dimethyl sulfate (1.6 ml, 2 g) and *p*-nitro-*N*,*N*-dimethylaniline (2.0 g) were heated with stirring on a steam bath for 7.5 h. The mixture was cooled, the product triturated with water, and filtered. Picric acid dissolved in water was added to the aqueous filtrate, the resulting picrate filtered and dried, yielding 2.1 g, mp 179-182 °C (lit.[38] 182-183 °C). The picrate (315 mg) was stirred at room temperature in concentrated hydrochloric acid for 1 h, the solution extracted three times with ether, and the water removed in vacuo. The residue was recrystallized three times from absolute ethanol-ether to give 30 mg of pure white needles of VIII, mp 180-182 °C (lit.[38] 183-184 °C).

***m*-Nitrophenyltrimethylammonium Chloride (IX).** Compound IX was prepared analogously to VIII, mp 235-235.5 °C (lit.[38] 230-235 °C).

***m*-Nitrophenyltrimethylammonium Iodide (X).** To an aqueous solution of IX was added an aqueous solution of NaI. The resulting precipitate was filtered and recrystallized from water, mp 189-190 °C.

***m*-Nitrophenyltrimethylammonium Perchlorate (Xa).** To an aqueous solution of IX was added 70% perchloric acid. The resulting precipitate was filtered and recrystallized from water, mp 231-232 °C.

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 (24 h at 200 °C in vacuo) 4A molecular sieves (MCB). Alternatively, spectrograde acetonitrile (MCB) was treated with dry molecular sieves. The water content from either of these procedures was 1 mM or less.

Tetraethylammonium perchlorate (TEAP) was prepared by dissolving tetraethylammonium bromide in boiling water and adding 70% 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.[39] 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 in the GC. The water content was determined by comparison of the area of the peak to that of a known concentration of methanol.[39] Water concentration in the cell was found to be 5-10 mM and determinations were considered accurate to ±1 mM.

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

The platinum bead electrode was cleaned with aqua regia before each use. The DME used in the majority of this study 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 DME used for the reduction of VI was characterized by $m^{2/3}t^{1/6} = 1.54$ and $m = 1.22$ mg/s at 45 cmHg; at 55 cmHg, $m^{2/3}t^{1/6} = 1.82$ and $m = 1.71$ mg/s; at 65 cmHg, $m^{2/3}t^{1/6} = 2.05$ and $m = 2.19$ mg/s. The electrochemical cell has been described previously.[40]

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

EPR. The cell for the in situ generations was constructed as follows. A ₮40/50 male joint was sealed at its base to a 5-mm o.d. glass tube about 13 cm long, which was in turn joined to a 5-cm length of 2-mm o.d. glass tube. A heavy gauge platinum wire was sealed into the 2-mm tube such that about 1 cm projected into it. The cathode was soldered to a thin copper wire external to the cell. The female portion of the ₮40/50 joint contained three ₮10/14 female joints for the anode, silver wire reference electrode, and degassing capillary. The latter was a long thin tube reaching to the bottom of the cell. Bethlehem instrumental grade mercury was dropped into the cell to cover the platinum wire and act as the electrode. A quantity of 2 ml of solution was used in each experiment. Concentration of TEAP was ~0.1 M, while the compounds were usually about 2 mM. The solutions were degassed with dry N_2 for 30 min before use. After degassing, the capillary was removed and replaced with a ground glass stopper (₮10/14). The solutions were electrolyzed 0.2-0.3 V negative to the $E_{1/2}$.

Acknowledgment. Financial support of this investigation by the National Science Foundation is gratefully acknowledged. We would like to thank Professor L. G. Pederson for assistance in carrying out the CNDO calculations.

References and Notes

(1) Alfred P. Sloan Fellow, 1973-1975; author to whom correspondence should be sent. Present address: North Dakota State University, Fargo, North Dakota 58102.
(2) H. R. Allcock, *Chem. Rev.*, **72**, 87 (1972); K. A. R. Mitchell, *ibid.*, **69**, 157 (1969); T. B. Brill, *J. Chem. Educ.*, **50**, 392 (1973); R. F. Hudson, *Rev. Pure Appl. Chem.*, **9**, 371 (1964); W. Shafer, A. Sweig, G. Markel, H. Hauptmann, and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, **12**, 145 (1973), and references cited therein.
(3) D. P. Craig and K. A. R. Mitchell, *J. Chem. Soc.*, 4682 (1965).
(4) M. J. S. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J. Chem. Soc.*, 2423 (1960).
(5) M. C. R. Symons, personal communication.
(6) H. R. Allcock, "Phosphorus-Nitrogen Compounds", Academic Press, New York, N.Y., 1972.
(7) J. J. Daly and G. Märkl, *Chem. Commun.*, 1057 (1969).
(8) S. F. Mason, *Nature (London)*, **208**, 495 (1965).
(9) R. Vllceanu, A. Balint, and Z. Simon, *Nature (London)*, **217**, 61 (1968).
(10) H. Oehling and A. Sweig, *Tetrahedron Lett.*, 4941 (1970).
(11) W. Shafer and K. Dimroth, *Angew. Chem., Int. Ed. Engl.*, **12**, 1753 (1973).
(12) A. R. Lyons, G. W. Neilson, and M. C. R. Symmons, *J. Chem. Soc., Faraday Trans. 2*, 807 (1972).
(13) A. R. Lyons and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 622 (1972).
(14) R. Hoffmann, D. B. Boyd, and S. Z. Goldberg, *J. Am. Chem. Soc.*, **92**, 3929 (1970).
(15) H. Absar and J. R. Van Wazer, *J. Am. Chem. Soc.*, **94**, 2382 (1972).
(16) R. D. Rieke and R. A. Copenhafer, *Electroanal. Chem. Interfac. Electrochem.*, **42**, 309 (1973).
(17) R. D. Rieke, R. A. Copenhafer, A. M. Aguiar, M. S. Chattha, and J. C. Williams, Jr., *J. Chem. Soc., Chem. Commun.*, 1130 (1972).
(18) J. H. Wagenknecht, Ph.D. Dissertation, State University of Iowa, 1964.
(19) J. H. Wagenknecht and M. Baizer, *J. Org. Chem.*, **31**, 3885 (1966).
(20) L. Horner and A. Mentrup, *Justus Liebigs Ann. Chem.*, **646**, 65 (1961).
(21) L. Horner and J. Haufe, *Chem. Ber.*, **101**, 2903 (1968).
(22) L. Horner and J. Haufe, *J. Electroanal..Chem.*, **20**, 245 (1969).
(23) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman, and P. Beck, *Tetrahedron Lett.*, 161 (1961).
(24) H. Matschiner and K. Issleib, *Z. Anorg. Allg. Chem.*, 60 (1967).
(25) J. M. Savennt and S. K. Bink, *Bull. Soc. Chim. Fr.*, 3549 (1972).
(26) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(27) A. J. Fry, "Synthetic Organic Electrochemistry", Harper and Row, New York, N.Y., 1972, p 36.
(28) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).
(29) J. Tomes, *Collect. Czech. Chem. Commun.*, **9**, 12 (1937).
(30) "Instruction Manual Polarographic Analyzer", Princeton Applied Research, Princeton, New Jersey, 1971, pp V10-V6.
(31) D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).
(32) K. Dimroth, *Fortschr. Chem. Forsch.*, **38**, 1 (1973).
(33) See C. K. White, Ph.D. Thesis, University of North Carolina, Chapel Hill, N.C., 1974, for details.
(34) P. H. Reiger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).
(35) R. G. Griffin, Ph.D. Dissertation, Washington University, St. Louis, Mo., 1968.
(36) L. Fox, Ph.D. Dissertation, University of North Carolina, Chapel Hill, N.C., 1973.
(37) L. Horner and H. Hoffman, *Chem. Ber.*, **91**, 45 (1958).
(38) A. Zaki and H. Fahim, *J. Chem. Soc.*, 2701 (1942).
(39) J. M. Hogan, R. A. Engel, and H. F. Stevenson, *Anal. Chem.*, **42**, 249 (1970).
(40) R. D. Rieke, W. E. Rich, and R. H. Ridgway, *J. Am. Chem. Soc.*, **93**, 1962 (1971).
(41) R. Rothuis, J. J. H. M. Fout Friede, J. M. F. van Dijk, and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **93**, 129 (1974).
(42) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).
(43) J. A. Pople and D. L. Beveridge, "Approximate M.O. Theory", McGraw-Hill, New York, N.Y., 1970.
(44) J. N. Brown, L. M. Trefonas, R. L. R. Towns, and R. Majeste, *J. Heterocycl. Chem.*, **7**, 8351 (1970).
(45) J. N. Brown and L. M. Trefonas, *J. Heterocycl. Chem.*, **9**, 35 (1972).
(46) J. N. Brown and L. M. Trefonas, *J. Heterocycl. Chem.*, **9**, 187 (1972).
(47) Available from Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.
(48) C. A. Coulson, *Nature (London)*, **221**, 1106 (1969).
(49) L. S. Bartel, L. S. Su, and H. Yow, *Inorg. Chem.*, **9**, 1903 (1970).