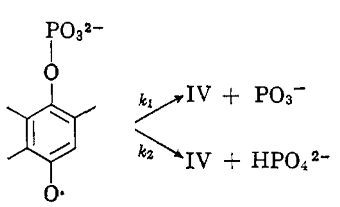

(11)

(12)

best separation between the two successive charge-transfer controlled steps. The rate data suggest the following pathways for the hydrolysis (eq 11 and 12), one independent of and one dependent on pH. The pH-independent pathway might produce a metaphosphate intermediate; hence the possible phosphorylating agent of biological interest is the semiquinone phosphate radical.

Acknowledgment. This research was supported by a Frederick Gardner Cottrell grant; Research Corporation is gratefully thanked for this support.

Examination of Phosphorus Hyperfine Coupling Constants in Nitroaromatic Anion Radicals[1a]

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Abstract: The electron spin resonance spectra of the anion radicals produced by electrochemical reduction of diethyl 4-nitrophenyl phosphate (**1**), O,O-diethyl O-4-nitrophenyl thiophosphate (**2**), diethyl 4-nitrobenzyl phosphonate (**3**), diphenyl 4-nitrophenyl phosphate (**4**), diphenyl 2,6-dimethyl-4-nitrophenyl phosphate (**5**), di(4-methylphenyl) 4-nitrophenyl phosphate (**6**), and di(2-methylphenyl) 4-nitrophenyl phosphate (**7**) have been examined. In every case, unequivocal assignment of a ^{31}P hyperfine coupling constant, a_P, was possible. The magnitude of a_P varied from 7.05 gauss for the radical derived from **1** in acetonitrile to 17.51 gauss for the radical derived from **3** in dimethylformamide. In all cases the values of the nitrogen and nitrophenyl ring proton coupling constants remained closely similar to those observed for nitrobenzene anion. The variation in values of a_P suggests that steric effects as well as inductive effects influence the ^{31}P coupling constant in these radicals and that at least some contribution of a hyperconjugative mechanism is likely for transmission of unpaired spin to the phosphorus atom.

Even superficial inspection of the recent chemical literature shows the rapid development of organophosphorus chemistry. Organophosphorus compounds have become increasingly important as intermediates in organic synthesis and as ligands in coordination chemistry. The central role of phosphate groups in photosynthesis, in nucleic acids, and in the energy-transfer processes of metabolism is well established.[2] Other phosphates are some of the most virulent poisons known. Some fluorinated phosphates are nerve gases and other phosphate and thiophosphate esters are widely used as pesticides.

Despite the fact that free-radical intermediates have frequently been postulated for organophosphorus reactions, comparatively few phosphorus-containing radicals have been prepared in solution under conditions which permitted their study in detail. Many of these radicals are apparently highly reactive and cannot be obtained in concentrations sufficient for characterization. Thus, in 1953, Hein[3] noted that the reaction of alkali metals with phosphine oxides led to colored, paramagnetic solutions, but he reported no specific data. Ramirez[4] observed electron spin resonance (esr) signals from intermediates in the reaction of triphenylphosphine with chloranil, but was able to report only that the radical species had a *g* factor close to 2. Other workers have reported phosphorus-containing radicals in irradiated solids[5-7] and at liquid nitrogen temperatures.[8]

Considerable attention has been devoted to attempts to prepare the anion radical of triphenylphosphine. Two reports of esr spectra resulting from alkali metal reduction of triphenylphosphine in tetrahydrofuran exist in the literature.[9,10] Assignments of these spectra to the triphenylphosphine anion did not, however, appear unequivocal since Chapman[11] had found only signals which he attributed to the biphenyl anion when triphenylphosphine was reduced with sodium–potassium alloy in dimethoxyethane. Recently Britt and Kaiser[12] have shown that the reaction of alkali metals with triphenylphosphine in tetrahydrofuran proceeds in two steps. In the first step a phenyl group is cleaved yielding a metal phenide and a metal diphenyl phosphide. Further reduction of the metal diphenyl

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(1) (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965; (b) abstracted in part from the Ph.D. Thesis of W. M. G., Cornell University, 1965; (c) Alfred P. Sloan Foundation Fellow.

(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962.

(3) F. Hein, H. Plust, and H. Pohlemann, *Z. Anorg. Allgem. Chem.*, **272**, 25 (1953).

(4) F. Ramirez and S. Dershowitz, *J. Am. Chem. Soc.*, **78**, 5614 (1956).

(5) J. R. Morton, *Can. J. Phys.*, **41**, 706 (1963).

(6) A. Horsfield, J. R. Morton, and D. H. Wiffen, *Mol. Phys.*, **4**, 475 (1962).

(7) M. Hanna and L. Altman, *J. Chem. Phys.*, **36**, 1788 (1962).

(8) U. Schmidt, F. Geiger, A. Muller, and K. Maricau, *Angew. Chem.*, **75**, 640 (1963).

(9) M. Hanna, *J. Chem. Phys.*, **37**, 685 (1962).

(10) M. Kabachnik, V. Voevodskii, T. Mastryukova, S. Solodovnikov, and T. Melenteva, *Zh. Obshch. Khim.*, **34**, 3234 (1964).

(11) D. Chapman, S. Glarum, and A. Massey, *J. Chem. Soc.*, 3140 (1963).

(12) A. D. Britt and E. T. Kaiser, *J. Phys. Chem.*, **69**, 2775 (1965); see also A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, **31**, 112 (1966).

Table I. Electrochemical Data

	CH_3CN				DMF		
Compound	$-E_{1/2}$, v[a]	i_d/C, μa mM^{-1}	$-(E_{3/4} - E_{1/4})$, mv	I[c]	$-E_{1/2}$, v[a]	i_d/C, μa mM^{-1}	$-(E_{3/4} - E_{1/4})$, mv
1	1.07_4	2.93	78	2.6	0.97_1	2.91	104
2	1.11_6	4.18	53	3.6	1.11_6	2.62	54
3	1.17_0	3.74	64	3.3	1.14_0	2.55	56
4	1.09_8	3.92	57	3.4	1.06_4	2.59	57
5	1.14_5	3.19	56	2.8			
6	1.09_2	4.77	57	4.2			
7	1.10_0	3.52	55	3.1			
8	0.86_5	4.64	71	4.0			
	1.21_1	3.81	68	3.3			
Nitrodurene	1.44_2[b]	4.35	56[b]	3.8[b]			

[a] Half-wave potentials measured *vs.* aqueous saturated calomel electrode. [b] Data from ref 21. [c] $I = i_d/m^{2/3}t^{1/6}C$, here computed from i_d/C values and I value for nitrodurene from ref 21.

phosphide then results in formation of the anion radical which gives rise to the esr signals previously attributed to the triphenylphosphine anion.

Muller and co-workers[13–15] and Lucken[16] appear to have obtained the first unambiguous esr spectra of phosphorus-containing free radicals. Muller, *et al.*,[13,14] found that derivatives of diphenyl(4-hydroxy-3,5-di-*t*-butylphenyl)phosphine could be dehydrogenated to obtain moderately stable radicals, while Muller, *et al.*,[15] and Lucken[16] have obtained esr spectra from phosphobetaines derived from substituted benzoquinones and triphenylphosphine. Coupling constants have been assigned to several of these compounds by these workers.

Arbuzov, *et al*,[17] have reported radicals generated by oxidation of several phosphonohydrazines, but no coupling to the ^{31}P nucleus was observed in the esr spectra. More recently, Kabachnik, *et al.*,[10] have reported esr spectra of several phosphine and phosphine oxide radicals produced by potassium reduction of the compounds in tetrahydrofuran. Allen and Bond[18] have reported esr spectra of radicals produced by the oxidation of several quinol phosphates with potassium permanganate.

The compounds selected for this study are 4-nitrophenyl derivatives of the respective phosphorus compounds. These compounds were chosen in order to take advantage of the stability of nitroaromatic anions and the fact that both the electrochemical behavior and esr spectra of numerous such radicals have been studied extensively.[19–21]

Experimental Section

Reagents. Acetonitrile, N,N-dimethylformamide (DMF), and tetraethylammonium perchlorate were prepared as described previously.[21,22] Diethyl 4-nitrophenyl phosphate (**1**) and O,O-diethyl O-4-nitrophenyl thiophosphate (**2**) were obtained from K & K Laboratories. Compound **1** was purified by vacuum distillation, and a fraction having the literature refractive index was used in this study. Diethyl 4-nitrobenzyl phosphonate (**3**), 4-nitrophenol, diphenyl chlorophosphate, di-*o*-tolyl chlorophosphate, di-*p*-tolyl chlorophosphate, and 4-nitrobenzyl alcohol were supplied by Aldrich Chemical Co. Triethylamine and mucobromic acid were obtained from Distillation Products Industries, and 3-pentanone came from Matheson Coleman and Bell.

Diphenyl 4-Nitrophenyl Phosphate (4). Reaction of equimolar quantities of 4-nitrophenol and diphenyl chlorophosphate in ether solution in the presence of a 10% molar excess of triethylamine resulted in precipitation of triethylamine hydrochloride which was removed by filtration. The filtrate was extracted with several portions of distilled water and then evaporated to yield the phosphate. The crude product obtained in 80% yield was recrystallized twice from ethanol. The resulting white crystals melted at 49–51°. This compound has apparently not previously been reported. The composition is confirmed by elemental analysis. *Anal.* Calcd for $C_{18}H_{14}NO_6P$: C, 58.23; H, 3.80; N, 3.77; P, 8.34. Found: C, 58.19, 58.44; H, 3.78, 3.86; N, 3.84, 3.89; P, 8.45, 8.22.

Diphenyl 2,6-Dimethyl-4-nitrophenyl Phosphate (5). Sodium nitromalonaldehyde monohydrate was prepared by reaction of sodium nitrite with mucobromic acid as described by Fanta.[23] 2,6-Dimethyl-4-nitrophenol was then obtained by condensation of 3-pentanone with the nitromalonaldehyde according to the method of Hill[24] as described by Jones and Kenner.[25] Phosphorylation of the phenol in the manner described above produced the phosphate in 18% yield. After recrystallization from ethanol, the product melted at 72–73°. This compound does not appear to have been prepared previously. The composition is established by elemental analysis. *Anal.* Calcd for $C_{20}H_{18}NO_6P$: C, 60.17; H, 4.54; N, 3.51; P, 7.76. Found: C, 60.05, 60.11; H, 4.63, 4.54; N, 3.50, 3.50; P, 7.61.

Di(4-methylphenyl) 4-Nitrophenyl Phosphate (6) and Di(2-methylphenyl) 4-Nitrophenyl Phosphate (7). Reaction of 4-nitrophenol with the appropriate chlorophosphate in the manner described gave **6** and **7**, respectively, in high yield. Both compounds were recrystallized from ethanol; **6** melted at 83–87° and **7** at 60–61°. Both of these compounds are isomeric with **5**, and since they appear not to have been prepared previously their compositions are confirmed by elemental analyses. *Anal.* Found for **6**: C, 58.40, 58.20; H, 4.06, 4.23; N, 4.13, 4.27; P, 7.54, 7.50. Found for **7**: C, 60.90, 60.90; H, 4.76, 4.51; N, 3.68, 3.78; P, 7.87, 7.78.

Diphenyl 4-Nitrobenzyl Phosphate (8). Phosphorylation of 4-nitrobenzyl alcohol as described above for **4** yielded **8**. After two recrystallizations from ethanol, this material melted at 65°, which is in agreement with the melting point reported by Mason and Todd[26] for a pure sample.

Polarography. Polarographic measurements were made with the ORNL three-electrode polarograph described earlier.[22] Experiments were performed at approximately 25°, and maximum currents are reported. Potential measurements were made *vs.* the aqueous saturated calomel electrode under conditions of "long immersion";[21] the precision of such measurements is presumed to be ±5 mv. Values of i_d/C were measured for all the compounds in Table I with a single capillary. Values of the diffusion

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(13) E. Muller, H. Eggensperger, and K. Scheffler, *Z. Naturforsch.*, **16b**, 764 (1961).

(14) E. Muller, H. Eggensperger, and K. Scheffler, *Ann. Chem.*, **658**, 103 (1962).

(15) E. Muller, H. Eggensperger, B. Teissier, and K. Scheffler, *Z. Naturforsch.*, **18b**, 984 (1963).

(16) E. A. C. Lucken, *ibid.*, **18b**, 166 (1963).

(17) A. Arbuzov, F. Valitova, A. Il'yasov, B. Kozyrev, and Yu. Yablokov, *Dokl. Akad. Nauk SSSR*, **147**, 839 (1962).

(18) B. Allen and A. Bond, *J. Phys. Chem.*, **68**, 2439 (1964).

(19) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(20) A. H. Maki and D. H. Geske, *ibid.*, **83**, 1852 (1961).

(21) D. H. Geske, J. Ragle, M. Bambenek, and A. Balch, *ibid.*, **86**, 987 (1964).

(22) K. Kuwata and D. H. Geske, *ibid.*, **86**, 2101 (1964).

(23) P. Fanta, *Org. Syn.*, **32**, 95 (1952).

(24) H. B. Hill, *Am. Chem. J.*, **24**, 1 (1900).

(25) E. Jones and J. Kenner, *J. Chem. Soc.*, 1842 (1931).

(26) H. Mason and A. Todd, *ibid.*, 2267 (1961).

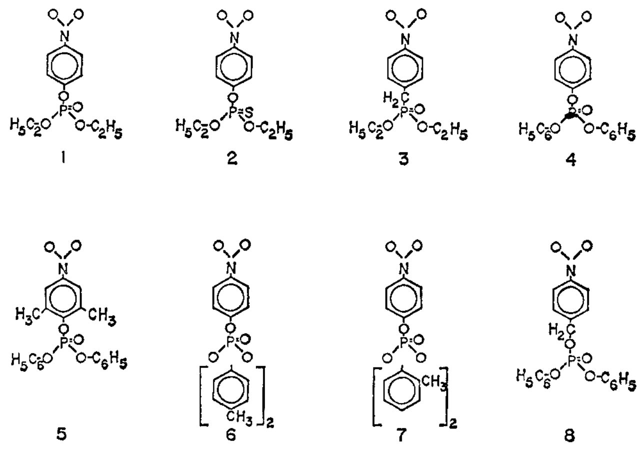

Figure 1. Molecular formulas of the compounds studied.

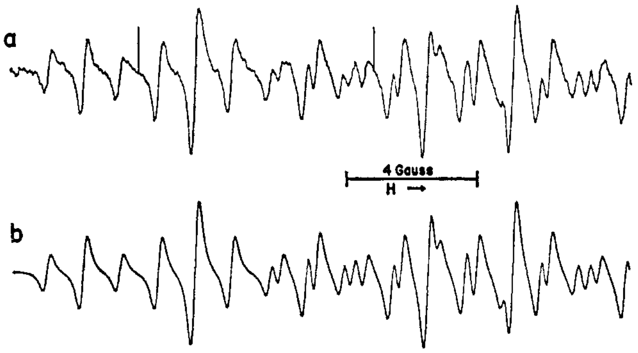

Figure 2. (a) First derivative esr spectrum of the anion radical produced by electroreduction of an approximately 2 mM solution of **1** in DMF. The low-field half of the spectrum is shown. (b) Computed spectrum using a_N = 9.93, a_H = 3.47 and 1.13, a_P = 7.28 gauss, and 0.230-gauss line width.

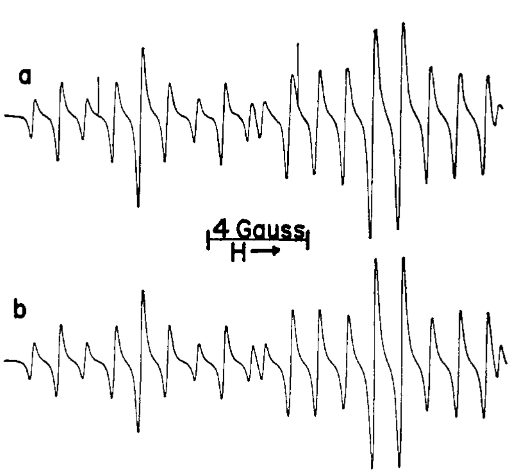

Figure 3. (a) First derivative esr spectrum of the anion radical produced by electroreduction of 1.6 mM solution of **2** in DMF. The low-field half of the spectrum is shown. (b) Computed spectrum using a_N = 9.68, a_H = 3.46 and 1.135, a_P = 10.82 gauss, and 0.185-gauss line width.

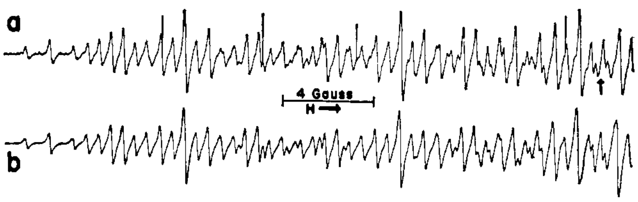

Figure 4. (a) First derivative esr spectrum of the anion radical produced by electroreduction of a 0.46 mM solution of **3** in DMF. Slightly more than the low-field half of the spectrum is shown. The center of the spectrum is indicated by the arrow. (b) Computed spectrum using a_N = 9.70, a_H = 3.34, 1.08, and 2.79, a_P = 17.60 gauss, and 0.140-gauss line width.

current constant, I, were then calculated for the phosphates using the value of 3.8 μa mM^{-1} mg$^{-2/3}$ sec$^{1/2}$ for nitrodurene as given in ref 21.

Electron Spin Resonance. Esr experiments were performed using the Varian V-4502 X-band spectrometer described previously.[22] Magnetic field measurements were made with a Harvey-Wells G-502 proton resonance gaussmeter. Radicals were produced in the resonance cavity by electrolytic reduction at a mercury cathode using the *intra muros* technique of Geske and Maki.[19]

Coupling constants were assigned to the spectra in a straightforward manner. These assignments have been confirmed by comparison of the experimental spectra with spectra calculated using a slightly modified version of the SESRS program[27] which was executed on a Control Data Corporation 1604 computer. Ring proton coupling constants have been assigned to molecular positions in analogy to the numerous nitrobenzene systems in the literature;[19,20] molecular positions are specified hereafter with reference to the nitro group.

Results

Compounds **1–7**, Figure 1, showed reproducible polarographic reduction waves in the potential region anticipated for substituted nitrobenzenes. **8** was reduced at substantially more anodic potentials, and, as discussed below, apparently the reduced species undergoes immediate decomposition. The values of the diffusion current constant obtained for each reduction wave are consistent with the transfer of one electron. It is not surprising that these compounds have somewhat smaller values of i_d/C than does nitrodurene since they are much larger molecules. Electrochemical data are summarized in Table I.

The apparently large discrepancy between the values of $E_{1/2}$ and $E_{3/4} - E_{1/4}$ for diethyl 4-nitrophenyl phosphate (**1**) in acetonitrile and those observed in DMF can be traced to the presence of a prewave in the former solvent even using freshly distilled solute. The absence of the prewave in DMF suggests that it is due to adsorption effects rather than impurities.

Esr data are summarized in Table II. Coupling constants reported are averages of high- and low-field branches of two or more spectra. The experimental esr spectra for the anion radicals observed for **1–5** in DMF solution and corresponding simulations are shown in Figures 2–6. Spectra of **6** and **7** were very similar to that of **4** and are omitted for brevity. Comparable agreement between experimental and calculated spectra was achieved for radicals in acetonitrile. Each simulation was obtained using coupling constants and line widths measured from the single experimental spectrum presented and these values are noted in the figure captions. This procedure was employed to achieve a better fit of the simulations since there were small variations in coupling constants from spectrum to spectrum as is apparent from the standard deviations reported in Table II.

In no case were further hyperfine lines resolvable. Lebedev, *et al.*,[28] have shown that, for Lorentzian lines,

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[27] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

[28] Y. Lebedev, D. Chernikova, and N. Tikomirova, *Zh. Strukt. Khim.*, **2**, 690 (1961).

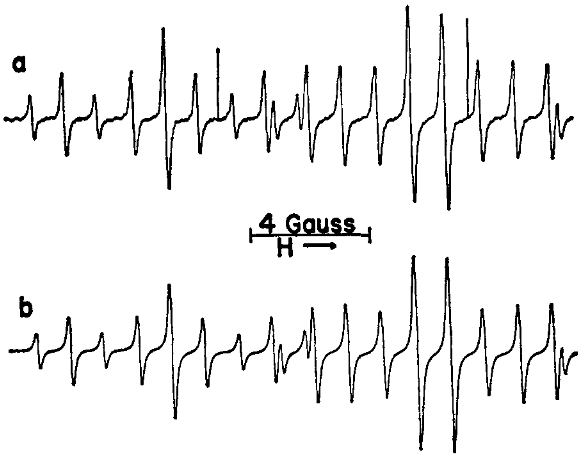

Figure 5. (a) First derivative esr spectrum of the anion radical produced by electroreduction of a 0.37 m*M* solution of **4** in DMF. The low-field half of the spectrum is shown. (b) Computed spectrum using $a_N = 9.46$, $a_H = 3.46$ and 1.12, $a_P = 8.31$ gauss, and 0.120-gauss line width.

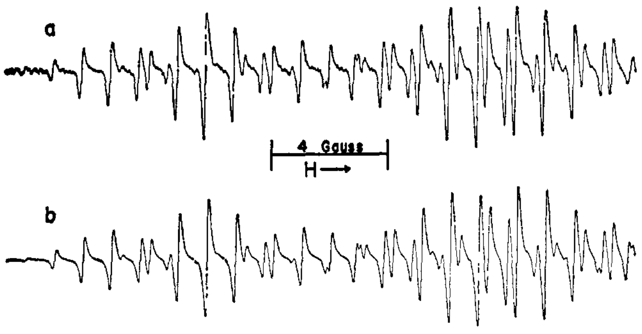

Figure 6. (a) First derivative esr spectrum of the anion radical produced by electroreduction of a 0.54 m*M* solution of **5** in DMF. The low-field half of the spectrum is shown. (b) Computed spectrum using $a_N = 9.71$, $a_H = 3.395$ and 1.02, $a_P = 11.06$ gauss, and 0.125-gauss line width.

the line width must be greater than 1.4 times concealed hyperfine splitting to avoid obvious distortion of the line shape. Thus, the observation of lines as narrow as 0.120 gauss in spectra of solutions sufficiently dilute to avoid concentration broadening together with excellent fit of line shapes by computer simulation suggest that protons in the ester groups couple very weakly, if at all. Although there is no unambiguous way to assign the coupling constants due to the *ortho* protons and *p*-methylene protons of radical **3**, short of selective deuteration, assignment of the larger value to the *ortho* position is consistent with (a) other compounds in this series, (b) the direction of change in going from acetonitrile to DMF, and (c) the magnitude of the methylene and methine proton coupling constants observed for the anion radicals of 4-ethyl- and 4-isopropylnitrobenzene.[29] Despite the moderately irreversible electrochemical behavior of **1**, the fit of the esr spectrum leaves no doubt regarding the identity of the radical.

No esr signals were detected when **8** was reduced at potentials corresponding to the first polarographic reduction wave. Electrolysis at potentials corresponding to the *second* polarographic wave produced weak esr signals, but the spectra appeared to change with time. Most of these spectra contained a center line and were, therefore, inconsistent with the presence of a unique nucleus of $I = {}^1/_2$ in the radical species. We are convinced that this paramagnetic species is not the anion radical of **8** but rather is the product of a secondary reaction.

Table II. Electron Spin Resonance Data[a]

Compound		Acetonitrile	DMF
1	a_N	10.43 ± 0.06	9.93 ± 0.03
	$a_{H(o)}$	3.64 ± 0.04	3.44 ± 0.04
	$a_{H(m)}$	1.13 ± 0.02	1.13 ± 0.02
	a_P	7.05 ± 0.06	7.28 ± 0.02
2	a_N	10.27 ± 0.04	9.71 ± 0.03
	$a_{H(o)}$	3.47 ± 0.02	3.46 ± 0.02
	$a_{H(m)}$	1.13 ± 0.02	1.12 ± 0.01
	a_P	10.29 ± 0.04	10.84 ± 0.02
3	a_N	10.26 ± 0.26	9.61 ± 0.19
	$a_{H(o)}$	3.33 ± 0.05	3.38 ± 0.02
	$a_{H(m)}$	1.10 ± 0.02	1.08 ± 0.05
	$a_{H(CH_2)}$	2.70 ± 0.02	2.81 ± 0.02
	a_P	13.59 ± 0.23	17.51 ± 0.24
4	a_N	9.96 ± 0.03	9.50 ± 0.03
	$a_{H(o)}$	3.42 ± 0.02	3.47 ± 0.02
	$a_{H(m)}$	1.12 ± 0.01	1.12 ± 0.01
	a_P	7.92 ± 0.02	8.35 ± 0.02
5	a_N	10.50 ± 0.04	9.75 ± 0.19
	$a_{H(o)}$	3.39 ± 0.01	3.40 ± 0.01
	$a_{H(m)}$	1.03 ± 0.01	1.02 ± 0.01
	a_P	10.50 ± 0.04	11.06 ± 0.06
6	a_N	10.14 ± 0.04	9.89 ± 0.03
	$a_{H(o)}$	3.46 ± 0.02	3.45 ± 0.02
	$a_{H(m)}$	1.12 ± 0.01	1.12 ± 0.01
	a_P	7.90 ± 0.02	8.00 ± 0.03
7	a_N	10.15 ± 0.06	9.87 ± 0.03
	$a_{H(o)}$	3.46 ± 0.01	3.46 ± 0.04
	$a_{H(m)}$	1.12 ± 0.02	1.12 ± 0.02
	a_P	8.27 ± 0.06	8.39 ± 0.03
Nitrobenzene[b]	a_N	10.32	9.83
	$a_{H(o)}$	3.39	3.32
	$a_{H(m)}$	1.09	1.09
	$a_{H(p)}$	3.97	3.97

[a] Absolute values of coupling constants are given in gauss, and standard deviations from the mean are indicated. Proton positions are labeled with respect to the nitro group. All the radicals in both solvents had a *g* factor close to 2. [b] Acetonitrile data from ref 19; DMF data from P. Ludwig, T. Layloff, and R. Adams, *J. Am. Chem. Soc.*, **86**, 4568 (1964).

Discussion

Esr Results. The nitrogen and proton coupling constants observed for the anion radicals derived from compounds **1–7** (Table II) indicate that the nitrophenyl group in each case is closely similar to nitrobenzene anion. This similarity to the unsubstituted radical provides clear evidence that the phosphorus-containing substituent has not grossly perturbed the π-electron spin density distribution in the nitrophenyl ring. Thus, from previous calculations,[30] it seems safe to assume that the π-electron spin density at the *para* carbon is about 0.17. With this small amount of spin available, it is relevant to consider the origin of the apparently large experimental phosphorus coupling constants.

It is well known that the magnitude of the splitting due to a particular nucleus depends upon both its nuclear spin moment and the value of the wave function $\psi^2 ns(0)$ evaluated at the nucleus for an appropriate s

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(29) T. M. McKinney, private communication.

(30) P. H. Reiger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

orbital. Morton[31] has tabulated these so-called "isotropic one-electron hyperfine constants" for a number of nuclei and reports a value of 10,178 Mc or 3630 gauss for a pure 3s electron associated with a ^{31}P nucleus. Thus, the largest phosphorus coupling constant observed in this study could be accounted for by a 3s spin density of only 0.0048. For comparison it may be noted that a_p for the PO_3^{2-} radical is 675 gauss.[7] It is, therefore, not difficult to rationalize the observed fact that the phosphorus coupling constants are relatively large while the spin densities in the nitrophenyl residue remain essentially unchanged.

We now wish to consider the changes in a_P which occur as the substituents on the nitrophenyl ring and on the phosphorus atom are altered. Comparison of the data for the radicals of **1** and **4** reveals that the replacement of ethyl groups by phenyl groups leads to relatively small changes in the coupling constants. Both electrochemical and esr data indicate that an ethyl group as a *para* substituent in nitrobenzene anion is electron donating[29] while a phenyl group is mildly electron withdrawing.[20] The slight changes in a_N for the anion radicals of **1** and **4** as compared with nitrobenzene anion do parallel the changes observed for the 4-ethylnitrobenzene and 4-phenylnitrobenzene anion radicals.[20,29] The small increase in a_P from radical **1** to radical **4** is thus qualitatively consistent with the change in the nature of the substituent group.

The comparison of radicals **1** and **2** is more clear-cut. Substitution of sulfur for the phosphoryl oxygen leaves a_N and ring proton coupling constants virtually unchanged but results in an increase in a_P of about 45%. Muller, *et al.*,[14] also noted an increase in a_P when a phosphoryl oxygen was replaced by a sulfur atom. They reported a phosphorus coupling constant of 14.7 gauss for the radical produced by dehydrogenation of diphenyl(4-hydroxy-3,5-di-*t*-butylphenyl)phosphine oxide and a phosphorus coupling constant of 15.4 gauss for the radical derived from the analogous phosphine sulfide. These workers[14] interpreted their data as indicative of an increase in the "positive" nature of the phosphorus atom in the sulfide. Alternatively, it can be noted that sulfur is less electronegative than oxygen and thus is a less effective electron "sink."

The largest ^{31}P coupling constant observed in this study was for the anion radical of **3**. It would, we feel, be a mistake to attribute this fact solely to the difference in the electronegativity of the atom connecting the aromatic ring and the phosphorus substituent, since the configuration of the radical may also be somewhat different.

A comparison of **3** and **8** is illustrative of the importance of the oxygen atoms in this type of compound. Thus, while radicals formed by electroreduction of **3** are exceedingly stable, no esr was observed when compound **8** was reduced on the first polarographic wave at room temperature. Similar behavior has been observed in the electroreduction of 4-nitrophenylacetonitrile; there is evidence that the carbon–hydrogen bonds of the methylene groups are labilized to such an extent by the electronegative cyano group that reduction takes place with rapid loss of a hydrogen atom to form a diamagnetic anion.[32] It is reasonable to suggest a similar phenomenon to explain the absence of esr signals from the one-electron reduction product of **8**. Since the substitution of phenyl for ethyl groups leads to only small changes in the properties of the radicals, the instability of the radical derived from compound **8** can be attributed to the extra oxygen atom.

Radicals of **4** and **5** differ only in the substitution of methyl groups for the ring protons at the two positions *meta* to the nitro group in the latter. This perturbation leads to an increase in a_N of approximately 5% and an increase in a_P of more than 30%. In view of the electron-donating character of methyl groups, it seems appropriate to ascribe the slight increase in a_N to a purely inductive effect. The possibility of a steric effect on a_P is examined subsequently.

Examination of molecular models suggests that the detailed nature of the ester group may alter the conformation of radicals. The isomeric radicals **6** and **7** were prepared to examine this possibility. Since both the reduction potentials and nitrogen coupling constants are identical within experimental uncertainty, we feel that the small increase in a_P in radical **7** over that in radical **6** is probably due to a steric effect (*vide infra*).

Phosphorus Spin Density. Consideration of the mechanism by which spin density is transmitted to the phosphorus atom in radicals **1–7** would most easily be done with full knowledge of the bond lengths and angles for the radicals. In the absence of such detailed data, we shall attempt to infer the radical geometry from the data that are available.

Pauling[33] notes that the observed P–O bond length in phosphate ion (PO_4^{3-}), 1.54 A, is 0.19 A shorter than that anticipated from covalent radii, and thus he infers a bond order of 1.70. Apparently, esterification perturbs the bond lengths since in triphenyl phosphate the P–X bond lengths are 1.63 and 1.43 A, where X represents successively the ester and phosphoryl oxygens. The O–P–O angle to the esterified oxygens varies between 101 and 117°, and the P–O–C angle is about 122°.[34] On this basis, it is reasonable to anticipate that the phosphorus atom in $(RO)_2P(O)OC_6H_4NO_2$ will be approximately tetrahedral with bond distances to the esterified oxygens of about 1.63 A and the remaining P–O bond somewhat shorter. This basic geometry of the phosphorus atom seems likely to be the same in all of the molecules we have examined. In the case of **3**, we anticipate that the P–CH_2–C angle is *ca.* 109°. Without evidence to the contrary, we presume that the geometry of the neutral molecules persists in the corresponding anion radicals.

The remaining structural question which is crucial to the question of spin transmission is the disposition of the C–Y–P plane with respect to the plane of the nitrophenyl group where C is the ring carbon atom and Y is a carbon or oxygen atom. Probably the most direct evidence on this question is available from the data for radical **3**. If the $-CH_2PO(OC_2H_5)_2$ substituent in this radical were rotating freely with respect to the nitrophenyl group, it is expected that the methylene proton coupling constant, a_{CH_2}, would be comparable to the methyl proton constant in the 4-nitrotoluene anion radical, *i.e.*, 3.98 gauss.[20] The fact that the observed value of a_{CH_2} for radical **3** is substantially

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[31] J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

[32] W. M. Gulick, Jr., unpublished results.

[33] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, pp 321–323.

[34] W. O. Davies and E. Stanley, *Acta Cryst.*, **15**, 1092 (1962).

smaller than 3.98 gauss could be used to argue that the preferred orientation of the $-CH_2PO(OC_2H_5)_2$ group places the phosphorus atom out of the plane of the aromatic ring. A similar argument was used by Stone and Maki[35] to rationalize the proton coupling constants for nitroalkane anion radicals in terms of a preferred orientation of the β protons with respect to the adjacent π plane. Such a treatment leads to the relation

$$a_H = \rho^\pi B\langle\cos^2\theta\rangle \qquad (1)$$

where ρ^π is the spin density on the sp^2-hybridized atom to which the alkyl group is attached, B is a constant, and θ is the angle between the C–H bond and the axis of the p_z orbital associated with the planar π-electron center, both projected on a plane perpendicular to the carbon–carbon bond. While the methylene proton coupling constants in **3** are indicative of conformation, the evidence must be regarded cautiously since the phosphorus substituent may also have perturbed a_{CH_2} by an inductive effect.

A more substantial test of the angular dependence of a_P is available from a comparison of the phosphorus coupling constants for the radicals of **4** and **5**. Examination of a molecular model of **4** suggests that the phosphate group *could* be freely rotating. This, of course, does not settle the question of what is actually happening in the anion. Introduction of methyl groups on the nitrophenyl ring di-*ortho* to the phosphate group leads to a clear preference in the molecular model for a conformation in which the phosphorus atom is out of the plane of the ring; one would, in fact, estimate $\langle\theta\rangle = 0°$ for the C–P bond of **5**. Although the configuration of radical **4** is not known in detail, it seems clear that the introduction of di-*m*-methyl groups produces a conformation which decreases the average value of θ. Likewise, we feel that the average value of θ is smaller for radical **7** than for radical **6** because of increased hindrance from the *o*-tolyl substituents in the former. The fact that a_P increases as the radicals are perturbed in the direction of smaller average values of θ, implies that the mechanism for transmission of spin density to the phosphorus atom embodies a dependence on θ, which *might* be of the form

$$a_P = C\langle\cos^2\theta\rangle \qquad (2)$$

An angular dependence is a natural consequence of a hyperconjugative mechanism. This mechanism was first suggested by Bersohn[36] as an explanation for the spin densities on methyl protons in methylated semiquinone radicals. Hyperconjugation amounts to a mixing of π orbitals of the π-electron system with the quasi π orbital formulated for the alkyl group.

Allen and Bond[18] have, in fact, rationalized the coupling constants in a series of semiquinone phosphate radicals in terms of a hyperconjugative mechanism.[37] They find that for a series of five semiquinone phosphate radicals with bulky groups *ortho* and di-*ortho* to the phosphate group, the phosphorus coupling constant ranged from 17.2 to 20 gauss. When a bulky group was not present, a "large" phosphorus coupling constant was not observed. In fact, Allen and Bond[18] asserted *no* phosphorus coupling constant was observed. Unfortunately, it was not possible to secure an unequivocal assignment of proton coupling constants for any of the semiquinone phosphates studied; thus, the identity of the unhindered radicals is open to question. These data do, at least, suggest that the phosphorus coupling constants are enhanced when the phosphorus atom is located away from the plane of the π-electron moiety. Carbon–phosphorus hyperconjugation appears to be a reasonable mechanism for transmission of spin density to the phosphorus atoms in radicals **1–7**.[38]

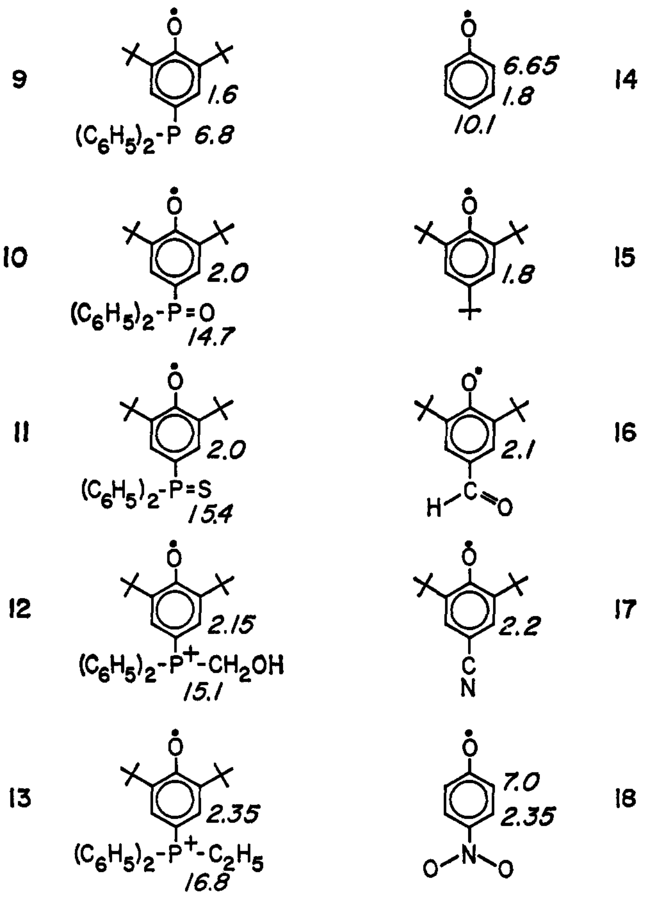

Figure 7. Coupling constants (in gauss) for substituted phenoxyl radicals from ref 14, 39, and E. Muller, K. Ley, K. Scheffler, and R. Mayer, *Ber.*, **91**, 2682 (1958).

As a matter of ancillary interest, we should like to comment on the data for the phosphorus radicals **9–13** as shown in Figure 7. Clearly the two isotropic coupling constants provide little basis for understanding the over-all π-electron spin density distribution. The phenoxyl radical (**14**), from which **9–13** are derived, only was observed in 1962[39] and thus could not form the

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(35) E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **37**, 1326 (1962).

(36) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(37) We do not agree with the conclusion of Allen and Bond[18] that no phosphorus coupling constant would be observed for a rapidly rotating phosphate group, but rather feel that the analogy with a methyl group is applicable. Indications are that methyl groups are freely rotating and finite methyl proton coupling constants surely have been observed.

(38) Carbon–carbon hyperconjugation has been documented experimentally by the recent work of L. M. Stock and J. Suzuki, *Proc. Chem. Soc.*, 136 (1962); *J. Am. Chem. Soc.*, **87**, 3909 (1965). A possible consequence of a hyperconjugative mechanism is that the phosphorus coupling constant would be temperature dependent. We have examined the esr spectra of radicals **4** and **5** over the temperature range 25 to $-45°$ and find no change in a_P within experimental uncertainty. At the lowest temperatures however, a_N was observed to be 3–4% larger than at room temperature in both radicals.

basis for comment by Muller, *et al.*,[14] in 1958. From the relation between a ring proton coupling constant, a_H, and spin density, ρ^π, at the contiguous carbon atom as expressed in[40]

$$a_H = -23.7\rho^\pi \qquad (3)$$

and the proton coupling constants in **14**, it is evident that a substantial fraction of the total spin density is on the benzene ring. In fact, the spin density at the *para* carbon atom in **14** is close to 0.4. On the basis of a number of theoretical calculations,[41] it now seems likely that the 1.8-gauss *meta* proton coupling constant, $a_{H(m)}$, for **14** arises from a negative spin density on the *meta* carbon atom, whereas the spin density at the *ortho* and *para* carbons is positive. It is only $a_{H(m)}$ that can be observed for trisubstituted radicals such as **15**. Introduction of electrophilic substituents such as -CN, -CHO, or $-NO_2$ is expected to *decrease* the spin density on the phenoxyl oxygen; comparison of $a_{H(m)}$ for **14** and **18** shows that the same perturbation increases the magnitude of the negative spin density at the *meta* carbon atom. Spin density at the *ortho* carbons may increase, as in **18**, but it need not necessarily increase on the *para* carbon atom.

Muller, *et al.*,[14] suggested that the parallel increase of $a_{H(m)}$ and a_P in the series **9** to **13** could be attributed to the positive (electrophilic) nature of the substituent. It now seems apparent that the change in $a_{H(m)}$ does correspond to a larger negative spin density on the *meta* carbon atom. This does not necessarily provide any information about the spin density on the *para* carbon atom, the important quantity in considering a spin polarization mechanism for transmission of spin density to the adjacent phosphorus atom.

In the group of radicals **9–13** radical **9** is distinguished by the fact that it is the only radical containing trivalent phosphorus. This fact may be fully as important in explaining the a_P of 6.8 gauss by comparison with values of 14.7–16.8 gauss for **10–13** as is the fact that the spin density on the oxygen atom apparently is somewhat larger than for **10–13**.[42]

It is likely that the mechanism for transmission of spin density to the phosphorus atoms in radicals **10–13** is different from the hyperconjugative mechanism proposed for the anion radicals of **1–7**.

Solvent Effects. In the anion radicals of **1**, **2**, **4**, **5**, **6**, and **7**, it is interesting that the sum of the nitrogen and phosphorus coupling constants for each radical happens to remain approximately constant when the solvent is changed from acetonitrile to DMF. The decrease in a_N and corresponding increase in a_P are interpretable in terms of an inductive effect due to the greater strength of the solvent complex with the oxygen atoms of the radical nitro group in acetonitrile.[43] Consequently, in DMF there is a shift of spin density toward the phosphate end of the ring. That the unique phosphoryl oxygen, unlike the nitro group oxygens, is not involved in the solvent effect to an observable extent is seen from a comparison of the data for radicals derived from **1** and **2**, since the exchange of sulfur for oxygen leads only to an increase in the value of a_P, but to no change in the magnitude or direction of the solvent effect. The magnitude of the solvent effect is about the same as that observed for *p*-alkyl-substituted nitrobenzene anions.[29] Radical **3**, however, shows a larger solvent effect, an increase in a_P of nearly 29% from acetonitrile to DMF as compared with changes of 1–5% for the other radicals.

Electrochemistry. In the past,[20] the half-wave potentials for reduction of *meta*-substituted nitrobenzenes have been correlated with the Hammett substituent constants, σ. A good correlation was also found for *para* substituents except where there was strong resonance interaction between the nitro group and the other substituent group.[20] If we choose to assume that such interaction is absent in compounds **1–4**, it is possible to calculate σ values for the various substituents on the basis of the half-wave potentials given in Table I. The calculated σ values appear in Table III. These values are surely approximate, but appear to be the first values obtained for organophosphorus substituents. In can be seen that they compare reasonably with the values obtained by Jaffé[44] for unesterified phosphates. Compounds **5** and **8** are not treated in this manner because of the complications which arise from multiple substitution on the benzene nucleus in one case and from the decomposition of the reduced species in the second case. In view of the close similarity of half-wave potentials for **4**, **6**, and **7**, the σ values for **6** and **7** would be essentially identical with that for **4**.

Table III

Compound	$\Delta E_{1/2}$, V[a] (CH_3CN)	σ_{calcd}	a_P (CH_3CN)
1	+0.073	0.250	7.05
2	+0.031	0.138	10.29
3	−0.023	−0.005	13.59
4	+0.049	0.186	7.92
		σ(*meta*)	σ(*para*)
$-PO_3H^-$[b]		0.25[c] 0.24[d]	0.17[c] 0.29[d]
$-PO_3^{2-}$[b]		−0.02	−0.16

[a] Computed from $\Delta E_{1/2} = (E_{1/2}^R - E_{1/2}^H)$ using the value of $E_{1/2}^H = -1.147$ for nitrobenzene obtained from ref 19. [b] Data from ref 44. [c] In water. [d] In 50% ethanol.

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(39) T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962); *J. Chem. Soc.*, 213 (1964).

(40) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(41) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964); N. M. Atherton, E. J. Land, and G. Porter, *Trans. Faraday Soc.*, **59**, 818 (1963); J. C. Schug, T. H. Brown, and M. Karplus, *J. Chem. Phys.*, **37**, 330 (1962); J. K. Becconsall, S. Clough, and G. Scott, *Trans. Faraday Soc.*, **56**, 459 (1960).

(42) J. R. Van Wazer, *J. Am. Chem. Soc.*, **78**, 5709 (1956).

(43) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962).

(44) H. Jaffé, L. Freedman, and G. Doak, *J. Am. Chem. Soc.*, **75**, 2209 (1953).