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Ligand Electronegativity Effect on the Spin Distribution in Phosphoranyl Radicals[1]

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Abstract: The trimethylphosphoranyl radical Me_3PH has been identified in γ-irradiated trimethylphosphine at −196° by means of its ESR spectrum consisting of an anisotropic ^{31}P doublet of isotropic ^1H doublets. Since this radical lacks electronegative groups which are thought to stabilize compounds and radicals of pentacoordinate phosphorus that assume trigonal bipyramidal geometry, the spin distribution is of particular interest. Comparison of the isotropic hyperfine splittings ($A_{iso}(^{31}P) = 484$ G; $A_{iso}(^1H) = 182$ G) with those obtained previously for alkoxyphosphoranyl radicals shows that the ^{31}P hfsc decreases monotonically on progressive substitution of the two apical alkoxy groups by alkyl or hydrogen ligands. In contrast, the large coupling to the hydrogen ligand in one apical position increases significantly when the other apical substituent is changed from an alkoxy to an alkyl group. These results indicate that the replacement of alkoxy groups by less electronegative ligands in the apical positions brings about a transfer of spin density from the orbitals of the central atom to the σ orbitals of the ligands leading to destabilization. This effect of electronegative substituents on the spin density distribution is in accord with the proposal that the half-occupied MO is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

A substantial body of ESR data now exists for a wide variety of phosphoranyl radicals,[2] and this information has naturally stimulated interest in the structure of this important class of intermediates.[3,4] Although many ESR studies have subscribed to the traditional view that the unpaired electron occupied essentially an equatorial sp^2 orbital of pentacoordinate (sp^3d hybridized) phosphorus in trigonal bipyramidal geometry, new light was shed on the electronic structure of these radicals by the recent finding[3] that large spin densities often reside in the σ orbitals of the axial ligands. While this latter result is difficult to reconcile with descriptions based on directed valence-bond theory, it becomes immediately understandable in terms of MO theory which assigns the unpaired electron in these radicals to an antibonding orbital of a_1 (C_{2v}) or a' (C_s) representation.[3] This orbital may be regarded as a three-center σ^* orbital derived from the axial ligand orbitals and the symmetry-allowed 3s and 3p orbitals of the phosphorus atom.

A corollary to this MO description is that the spin density distribution between the contributing group of ligand and central atom orbitals should be sensitive to the electronegativities of the ligands in the apical (axial) sites. In particular, the progressive replacement of two apicophilic electronegative groups by alkyl or hydrogen ligands should destabilize the radical,[3,5] the anticipated effect being to increase the spin populations on the apical ligands at the expense of the phosphorus atom.

Although the ESR spectra of a number of organophosphoranyl radicals with only one electronegative ligand (alkoxy) have been documented,[6] as yet the only ESR report describing a phosphoranyl radical without any electronegative ligands concerns the parent species PH_4.[7] However, the isotropic ^{31}P and ^1H splittings attributed to this radical appear to be quite anomalous and the identification has been seriously questioned.[8,9] In this paper we report the ESR spectrum and spin density distribution for the trimethylphosphoranyl radical thereby completing the set of ESR parameters for the series $R_nP(OR')_{4-n}$ (n = 0–4), where R is Me or H, and R′ is Me, Et, or t-Bu. Taken in conjunction with other work, our present results are shown to provide further evidence that the unpaired electron is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

Experimental Section

Samples of trimethylphosphine (Strem Chemicals Inc.) were prepared in Suprasil ESR tubes by standard high-vacuum techniques. Attempts were made to obtain single crystals by a low-temperature technique[10] but our efforts in this direction were frustrated by the apparent occurrence of a phase transition in the solid below the melting point (−85°) and only partially oriented samples could be obtained for studies at −196°. However, even the small degree of preferential orientation induced by this method proved to be valuable in locating the characteristic features of the powder ESR spectrum, as discussed below.

Table I. Isotropic ESR Parameters for Some Organophosphoranyl Radicals[a]

Radical	No. of alkoxy ligands	Temp, °C	$a(^{31}P)$, G	$a(^{1}H)$,[b] G	g
Me_3PH[c]	0	−196	484	182	2.0035
$MePH_2(OR)$[d]	1	−85	631.5	139.6	
$Me_2PH(OR)$[d]	1	−65	631.4	142.9	
Me_3POR[d]	1	−81	618.7		
$MePH(OR)_2$[d]	2	−85	703.3		
$Me_2P(OR)_2$[d]	2	−65	713.7		
$MeP(OMe)_3$[e]	3	−70	783.1		2.003
$MeP(OEt)_3$[e]	3	−70	786.7		2.004
$EtOP(OMe)_3$[e]	4	−70	884.0		2.003
$P(OR)_4$[f]	4	−70	918		2.004

[a] R = *t*-Bu. [b] Coupling to apical hydrogen ligand. [c] This work; the isotropic parameters were deduced from the anisotropic couplings given in the text and the values showed no significant change between −196° and the temperature (−135°) at which the radicals disappeared on annealing. [d] Reference 6. [e] Reference 15. [f] G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, 94, 8784 (1972).

Irradiations were carried out at −196° in a cobalt-60 γ source and the samples were transferred promptly into a liquid nitrogen dewar which fitted into the cavity of a Varian (V-4502-15) X-band ESR spectrometer. Spectra were recorded at sample temperatures above −196° by means of a variable-temperature accessory. Measurements of the magnetic field strength were made using a proton magnetic resonance probe (Walker/Magnemetrics Precision NMR Gaussmeter, Model G-502).

Results and Discussion

Figure 1 shows ESR spectra of γ-irradiated trimethylphosphine at −196° recorded at two orientations. Apart from the radical of interest to us here, the spectrum consists of the intense doublet due to the hydrogen atom (a = 507 G) and the outermost pair of features which are thought to be the (1, ±1) components of the dimer radical cation $Me_3P\text{-}PMe_3^+$ analogous to the species produced in γ-irradiated trimethyl phosphite.[11] The remaining features consisting of an anisotropic ^{31}P doublet of ^{1}H doublets are assigned to the Me_3PH radical, as indicated by the stick diagram. The integrity of this hyperfine structure was established by power saturation and annealing studies, as well as by the change of line shape with orientation.

The sample used to obtain the spectra of Figure 1 was polycrystalline but apparently possessed some degree of preferential orientation. This was useful because the intensity of the parallel (outer) features could be enhanced for some directions,[12] as illustrated in the upper spectrum. As expected, the resolution is somewhat better at high field because the second-order downfield shifts are greater for the perpendicular than for the parallel features in the case of $|A_\parallel| > |A_\perp|$.[13] After second-order corrections had been applied,[13] the ESR parameters were found to be $A_\parallel(^{31}P)$ = 537 G, $A_\perp(^{31}P)$ = 458 G, $A_\parallel(^{1}H)$ = 183 G, $A_\perp(^{1}H)$ = 181 G, $g_\parallel$ = 2.0054, and $g_\perp$ = 2.0026. The fairly small anisotropy associated with the smaller doublet splitting is fully consistent with the assignment to proton coupling.

The spin density distribution for the Me_3PH radical is shown in Figure 2. These values were derived in the usual way[3,11] from the isotropic and anisotropic components of the hyperfine couplings, viz., $A_{iso}(^{31}P)$ = 484 G, $2B(^{31}P) = \frac{2}{3}(A_\parallel(^{31}P) - A_\perp(^{31}P))$ = 53 G, and $A_{iso}(^{1}H)$ = 182 G. The sum of the spin densities in the hydrogen 1s orbital and the phosphorus 3s and 3p orbitals is 0.75, so in the light of previous work[3] it is reasonable to assume that most of the remaining spin density resides in the σ orbital of the apical methyl group which contributes to the MO occupied by the unpaired electron. A direct measurement of the spin density in this methyl orbital would require a determination of the ^{13}C hfs tensor but this was not feasible in the present study.

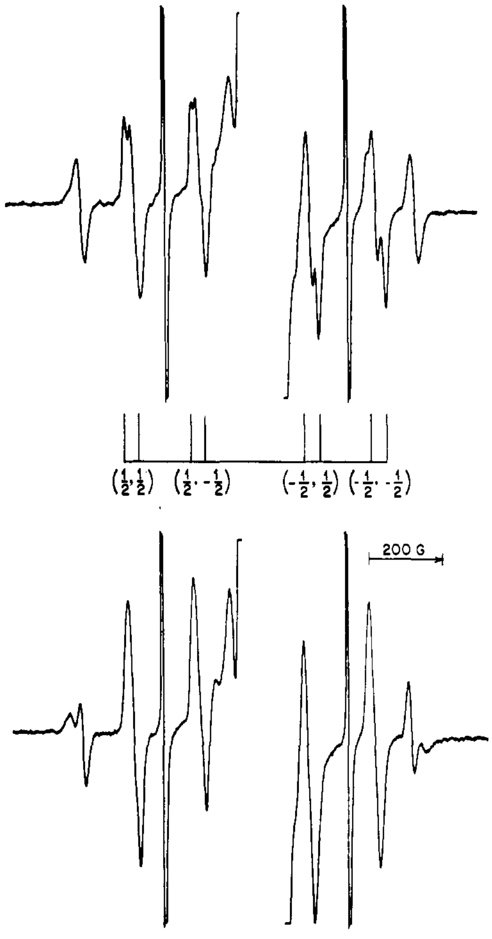

Figure 1. First-derivative ESR spectra of γ-irradiated trimethylphosphine at −196° recorded at two different orientations. The stick diagram refers to the parallel and perpendicular features of a ^{31}P doublet of ^{1}H doublets spectrum which is assigned to the Me_3PH adduct.

It is instructive to compare (Table I) the isotropic hyperfine splittings for Me_3PH with those obtained previously for alkoxyphosphoranyl radicals. Evidently, the replacement of the apical alkoxy group in monoalkoxyphosphoranyl radicals by hydrogen or methyl results in a marked decrease of the ^{31}P hfsc by ca. 140 G. This agrees with the previous trend along the series showing that the ^{31}P hfsc increases monotonically according to the number of alkoxy groups in the organophosphoranyl radical. Also of interest is the significant increase in the hyperfine splitting of the apical hydrogen on substituting the alkoxy group in $Me_2PH(OR)$ by methyl. In fact, the proton coupling of 182 G for Me_3PH appears to be the largest value ever reported for radicals other than H-atom complexes and corresponds to a hydrogen 1s spin density of 0.36.

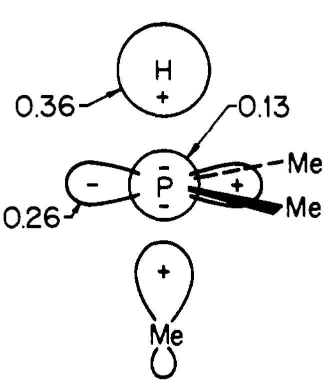

Figure 2. Molecular orbital occupied by the unpaired electron in the trimethylphosphoranyl radical. The values of the spin densities in the contributing atomic orbitals were calculated from the ESR data.

Therefore it appears that the destabilization incurred by the alkyl substitution of the alkoxy group in Me$_2$PH(OR) is manifested directly by a transfer of spin density from the phosphorus 3s orbital to the σ orbitals of the apical ligands. This is consistent with the antibonding character of the half-occupied three-center orbital in these radicals[3] and fully accords with our earlier expectations. Incidentally, these results must cast further doubt on the purported spectrum[7] of the PH$_4$ radical. Also, they reveal no indication of a marked change in the geometry of phosphoranyl radicals as the apical ligands become less electronegative.

In conclusion, it seems worthwhile to point out a simple implication of the three-center orbital description for the reactivity of phosphoranyl radicals.[14] It is natural to expect that as a greater spin density moves out from the phosphorus onto the apical ligands, so the lability of organophosphoranyl radicals to α scission should be increased. Since monoalkoxytrialkylphosphoranyl radicals undergo α scission quite readily with the loss of an alkyl radical,[6] this tendency should be even more pronounced for tetraalkylphosphoranyl radicals and might explain the difficulty of alkyl radical addition to trialkylphosphines[6] as compared with trialkyl phosphites.[15]

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Singlet Acetone Efficiency and Importance of Triplet Acetone Induced Decomposition of Tetramethyl-1,2-dioxetane from Direct Chemiluminescence[1]

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Abstract: From absolute emission intensities and decay lifetimes of the direct chemiluminescent decomposition of tetramethyl-1,2-dioxetane it was established that the singlet excited acetone yields (α) are 0.091 ± 0.033 and 0.05 ± 0.01% at 72 and 22°, respectively. The activation energy for tetramethyl-1,2-dioxetane thermolysis was 25 ± 2 kcal/mol, but the singlet yield (α) was independent of temperature. The induced decomposition efficiency (δ) of the 1,2-dioxetane by triplet acetone was found to be unity in the presence or absence of molecular oxygen, indicating that δ is independent of the lifetime of the triplet acetone sensitizer. The results for the direct chemiluminescent decomposition of tetramethyl-1,2-dioxetane implicate a mechanism in which sensitizing acetone triplets are efficiently replenished.

It has been demonstrated that the four-membered ring cyclic peroxide tetramethyl-1,2-dioxetane (TMD)[4] exhibits chemiluminescence on thermal decomposition. Consequently, this "high energy" molecule serves as the chemical energizer of electronically excited singlet and triplet acetone (eq 1). The salient features of this unusual process for TMD follow. Since some 25 kcal/mol activation energy is available: (i) enough chemical energy is stored in TMD to excite