Academician A. E. ARBUZOV, F. G. VALITOVA, A. V. IL' YASOV, B. M. KOZYREV,

Yu. V. YABLOKOV

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Abstract

Full Text

Academician A. E. ARBUZOV, F. G. VALITOVA, A. V. IL' YASOV, B. M. KOZYREV,
Yu. V. YABLOKOV

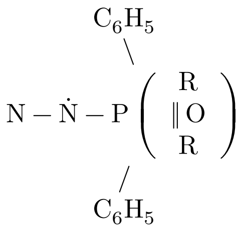
ELECTRON PARAMAGNETIC RESONANCE IN SOLUTIONS OF CERTAIN FREE RADICALS OF THE PHOSPHONHYDRAZYL SERIES

Investigation of free radicals of the hydrazyl series by the method of electron paramagnetic resonance (e.p.r.) showed that the unpaired electron is localized mainly on the nitrogen atoms of the hydrazyl ($^{1-5}$). The sum of the constants $A_1 + A_2$, characterizing the coupling of the unpaired electron with the nuclei of the α- and β-nitrogen atoms, proved to be equal to 17.52 oersted for α,α-diphenyl-β-picrylhydrazyl (DPPH) (^{3}) and deviates only slightly from this value for all its derivatives that have been studied.

It was found that the coupling of the unpaired electron with the nuclei of the two nitrogen atoms is unequal (^{6,7}). In the case of DPPH the ratio $A_1/A_2 = 0.77$, the larger constant belonging to the β-nitrogen atom (^{3}). Upon substitution in any part of the DPPH molecule the ratio of the constants changes; the smallest value, $A_1/A_2 = 0.47$, is observed for α,α-diphenyl-β-triphenylmethylhydrazyl (^{4}). When oxygen-free solutions of DPPH (^{3}) were used, it was found that there is a nonzero probability of finding the unpaired electron also on the aromatic rings. In the case of diphenyltriphenylmethylhydrazyl and diphenylpentaphenylcyclopentadienylhydrazyl, additional structure, attributed to the 2,4,6 protons of one of the α-phenyls, is also observed in solutions that have been only partially degassed (^{4,5}).

Fig. 1. E.p.r. spectrum of phosphonhydrazyl (I) in chloroform (*a*) and acetonitrile (*b*) solutions
($C = 0.001$ mol/l, $T = 300$°K)

In the present work an e.p.r. study is described of free radicals of the phosphonhydrazyl series with the general structural formula



$$\begin{array}{c} C_6H_5 \\ \backslash \\ N - \dot{N} - P \left(\begin{array}{c} R \\ \| O \\ R \end{array} \right) \\ / \\ C_6H_5 \end{array}$$

where I. $R = OC_2H_5$;

II. $R = OC_6H_5$; III. $R = C_6H_5$.

The indicated radicals proved to be unstable in air; they could not be isolated in the solid state. Phosphonhydrazyls (I)–(III) were obtained and studied in solutions of acetonitrile and chloroform. In nonpolar media (benzene, dioxane) the radicals could not be obtained.

The e.p.r. spectra were studied in partially degassed solutions with radical concentrations of $\sim 1 \cdot 10^{-3}$ mol/l. The measurements were carried out at room temperature on a standard RE-1301 radiospectrometer with an oscillating magnetic-field frequency $\nu = 9330$ MHz. In all the radicals studied there is observed a hyperfine structure [[unclear: abbreviated word]] of five equidistant lines, caused by interaction of the unpaired electron with two nitrogen atoms N^{14} (Fig. 1). The spectrum is described by the spin-

Hamiltonian

$$\hat{\mathscr{H}} = g\beta H\hat{S} + A_1\hat{S}\hat{I}_{N_1} + A_2\hat{S}\hat{I}_{N_2},$$

where $g \simeq g_{\text{DFPG}} = 2.0036$, β is the Bohr magneton, H is the value of the static magnetic field, $S = \frac{1}{2}$, and $I_{N_1} = I_{N_2} = 1$.

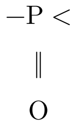
The determination of the constants A_1 and A_2, as well as of the width δH between the points of maximum and minimum of the first derivative of an individual h.f.s. line, was carried out by comparison with theoretically constructed curves with prescribed parameters. The theoretical curves were formed by summing nine h.f.s. lines, the superposition of which gives the observed spectrum. It was assumed that each line has a Gaussian shape and that the magnitude of the hyperfine splittings does not depend on the constant magnetic field. The calculations were carried out on an M-3M electronic computer. The values of $A_1 + A_2$, A_1/A_2, and δH given in Table 1 give the best agreement with the experimental curves.

Table 1

Parameters of the h.f.s. spectra of phosphonhydrazyls in solutions
($C = 1 \cdot 10^{-3}$ mol/l, $T = 300$°K)

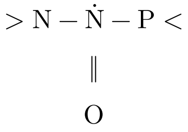
	Radical	Solvent	$A_1 +$ A_2, ±0.2 Oe	A_1/A_2	δH, ±0.2 Oe
I	$(C_6H_5)_2N-\dot{N}-P(=O)(OC_2H_5)_2$	Chloroform	10.2	0.97	3.9
I	$(C_6H_5)_2N-\dot{N}-P(=O)(OC_2H_5)_2$	Acetonitrile	11.4	0.97	3.6
II	$(C_6H_5)_2N-\dot{N}-P(=O)(OC_6H_5)_2$	Chloroform	10.8	0.97	4
II	$(C_6H_5)_2N-\dot{N}-P(=O)(OC_6H_5)_2$	Acetonitrile	11.2	0.97	3.9
III	$(C_6H_5)_2N-\dot{N}-P(=O)(C_6H_5)_2$	Chloroform	9.4	0.95	4.3
III	$(C_6H_5)_2N-\dot{N}-P(=O)(C_6H_5)_2$	Acetonitrile	10.6	0.95	3.6

As can be seen from Table 1, the sum of the constants $A_1 + A_2$ for phosphonhydrazyls proves to be appreciably smaller than for DFPG and its derivatives. This shows that part of the unpaired-electron density in the phosphorus radicals is transferred from the nitrogen atoms to other atoms. At the same time, the insignificant difference between the spectra of the radicals with phenoxy and ethoxy groups, and the absence of additional proton structure, show that this decrease cannot be explained by an increase in the delocalization of the unpaired electron over the peripheral parts of the molecule. It is therefore natural to consider that the decrease of $A_1 + A_2$ in phosphonhydrazyls in comparison with the value for DFPG is due to the group



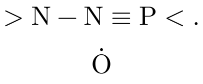
$$\begin{array}{c} -\mathrm{P}< \\ \| \\ \mathrm{O} \end{array}$$

In our experiments no h.f.s. from the P^{31} nucleus ($I = 1/2$) is observed. It may be thought that this occurs because of the small density of the unpaired electron at the phosphorus atom. In this case, in order to explain the decrease in the h.f.s. constants, it is necessary to assume that, along with the structure



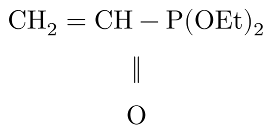
$$\begin{array}{c} >\mathrm{N}-\dot{\mathrm{N}}-\mathrm{P}< \\ \| \\ \mathrm{O} \end{array}$$

there exists, with sufficiently large weight, the structure



$$\begin{array}{c} >\mathrm{N}-\mathrm{N}\equiv\mathrm{P}<. \\ \dot{\mathrm{O}} \end{array}$$

However, in work (⁹) it was shown that in



$$\mathrm{CH_2 = CH -}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{(OEt)_2}$$

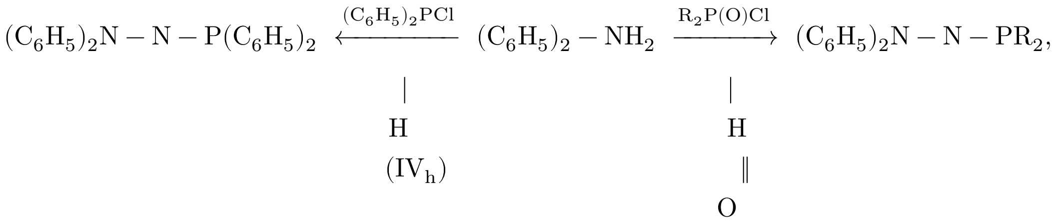
conjugation of the double bond $\mathrm{P=O}$ with the π-orbital of the $\mathrm{C=C}$ bond is unlikely, and the phosphorus–oxygen bond is polar to a considerable degree. Although a definitive answer regarding the density of the unpaired electron on the oxygen atom in our radicals can be given only by experiments with replacement of oxygen in the $\mathrm{P \to O}$ group by the isotope O^{17}, it seems to us more probable that the decrease in the density of the unpaired electron on the nitrogen atoms is due to

is determined precisely by the polarity of the $\mathrm{P \to O}$ bond. The influence of positively charged P^{31} may lead to a displacement of the unpaired-electron density from the nitrogen atom, which, in agreement with experiment, will be manifested in a decrease in $A_1 + A_2$ and in the equalization of A_1 and A_2. At the same time, the absence of h.f.s. from P^{31} is explained either by the small density of the unpaired electron on the phosphorus atom itself, or by insufficient S-hybridization of the wave function of this electron at the phosphorus atom. The difference in the values of $A_1 + A_2$ for radicals (I)–(III) can be explained by different changes in the polarity of the $\mathrm{P \to O}$ bond by the groups adjacent to phosphorus.

The study of the radicals obtained in various solvents showed that the e.p.r. spectrum depends appreciably on the nature of the solvent (Fig. 1). As can be seen from Table 1, narrowing of the hyperfine components and an increase in the h.f.s. constants are observed in the more polar solvent (acetonitrile) in comparison with δH and A for radicals in chloroform. Such an influence of the solvent on the e.p.r. spectrum was observed earlier (10) in some free radicals of another type and was explained by the formation of a solvation shell around the radical molecule. The latter affects the possibility of the occurrence of exchange interactions upon collisions of molecules, which, according to the Peik–Tattle mechanism (11,12), lead to broadening of the h.f.s. components. An explanation analogous to that given in (10) is probably also possible in the case of the phosphonhydrazyls studied.

Experimental Part

To obtain free radicals of the phosphonhydrazyl type, the corresponding phosphonhydrazines were synthesized. The latter were obtained by the action of unsymmetrical diphenylhydrazine (2 mol) on the corresponding acid chlorides of phosphates and phosphines (1 mol) in acetonitrile solution at room temperature. The initial acid chlorides were synthesized by the methods described in (13–15). The reaction proceeds according to the scheme



$$(C_6H_5)_2N-\underset{\substack{|\\ H}}{N}-P(C_6H_5)_2 \xleftarrow{(C_6H_5)_2PCl} (C_6H_5)_2-NH_2 \xrightarrow{R_2P(O)Cl} (C_6H_5)_2N-\underset{\substack{|\\ H}}{N}-\underset{\substack{\|\\ O}}{P}R_2,$$

(IV_h)

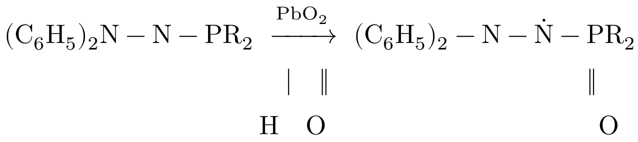
where R = OC_2H_5 (I_h), OC_6H_5 (II_h), or C_6H_5 (III_h), and is accompanied by a rise in temperature to 37-39° with abundant precipitation of crystals of diphenylhydrazine hydrochloride. On the following day, after removal of the crystals, the filtrate was concentrated in vacuo with a water-jet pump at room temperature. Dry ethyl ether was added to the residue obtained. In the case of hydrazines (II_h) and (III_h), a crystalline precipitate separated. Purification of the hydrazines was carried out by repeated dissolution in chloroform or acetonitrile and precipitation with dry ether. The results obtained and the analyses are given in Table 2.

α-Diethylphosphon-$\beta\beta$-diphenylhydrazine (I_h) is an oily liquid of bright-yellow color with a weak odor, boiling with decomposition at 140-150°/mm. To free (I_h) from diphenylhydrazine hydrochloride, washing with acetonitrile was used. α-Diphenylphosphon-$\beta\beta$-diphenylhydrazine (II_h) is obtained in the form of snow-white fluffy crystals with m.p. 133-134°. Usually, from concentrated solutions (in chloroform or acetonitrile), hydrazine (II_h) is isolated in a sufficiently pure state by precipitation with dry ether. Hydrazines (I_h) and (II_h) dissolve well in alcohol, benzene, chloroform, acetonitrile, dioxane, and acetic acid, with difficulty in dry ethyl ether, and are insoluble in water. Hydrazine (I_h) dissolves with a faint yellow coloration; solutions of hydrazine (II_h) are colorless. When dissolved in concentrated sulfuric acid, all hydrazines (I_h—IV_h) give a dark-blue coloration. The phosphonhydrazines obtained were oxidized in various solvents with lead dioxide by means of ···

Table 2

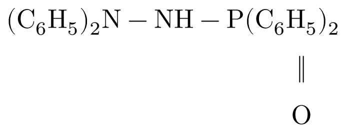
No.	Taken into reaction, g: chloroanhydride	Taken into reaction, g: $(C_6H_5)_2N-NH_2 \cdot HCl$	Obtained, g: phosphonhydrazine	Obtained, g: $(C_6H_5)_2N-NH_2 \cdot HCl$	Physical properties of the phosphonhydrazines	Yield, %	Empirical formula	P, % calculated	P, % found	N, % calculated	N, % found
1.	$(C_2H_5O)_2P(O)Cl$	7.9	$(C_6H_5)_2N-NH-P(O)(OC_2H_5)_2$ 13.7	3.8	Bright-yellow oily liquid d_4^{20} 1.169 n_D^{20} 1.5642	74	$C_{16}H_{21}N_2O_3P$	9.69	9.27	8.75	8.57
2.	$(C_6H_5O)_2P(O)Cl$	5	$(C_6H_5)_2N-NH-P(O)(OC_6H_5)_2$ 13.4	2.5	m.p. 133–134°C	75	$C_{24}H_{21}N_2O_3P$	7.47	7.54	6.73	6.70
3.	$(C_6H_5)_2P(O)Cl$	4	$(C_6H_5)_2N-NH-P(O)(C_6H_5)_2$ 12.7	2.2	m.p. 154–156°C	73	$C_{24}H_{21}N_2OP$	8.07	8.19	7.29	7.64
4.	$(C_6H_5)_2PCl$	8.2	$(C_6H_5)_2N-NH-P(C_6H_5)_2$ 15	4.8	Thick syrup of amber-yellow color	70	$C_{24}H_{21}N_2P$	8.42	8.59	7.61	7.38

according to the method described in (17). The oxidation reaction may be represented by the scheme:



$$(C_6H_5)_2N-\underset{H}{N}-\underset{O}{\overset{}{PR_2}} \xrightarrow{PbO_2} (C_6H_5)_2-N-\dot{N}-\underset{O}{PR_2}$$

In all cases the EPR signal appeared only 2–3 days after the start of oxidation. By this time the solutions acquire a reddish-brown color. We also synthesized phosphonhydrazines containing trivalent phosphorus. As was to be expected, in the course of oxidation of these compounds the trivalent phosphorus is converted into pentavalent phosphorus. This is evidenced by the fact that completely identical spectra are obtained from the oxidation products of diphenyl-β,β-diphenylhydrazinophosphine oxide



$$(C_6H_5)_2N-NH-\underset{\underset{\displaystyle O}{\|}}{P}(C_6H_5)_2$$

(III_n) and diphenyl-$\beta\beta$-diphenylhydrazinophosphine

$$(C_6H_5)_2N-NH-P(C_6H_5)_2$$

(IV_n). In this case compounds (III_n) and (IV_n) were oxidized under identical conditions.

Chemical Institute named after A. E. Arbuzov
Academy of Sciences of the USSR

Physico-Technical Institute of the Kazan Branch
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.