RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

June 1975

Translated from *Uspekhi Khimii*, **44**, 969-1002 (1975)

U. D. C. 541.67+546.18

Free Radicals Derived from Phosphorus Compounds

V.V.Pen'kovskii

Studies on phosphorus-containing free radicals and radical-ions are discussed in the review and data on the geometrical and electronic structures of phosphinyl, phosphonyl, and phosphoranyl radicals and radical-ions derived from compounds of tri-, tetra-, and penta-coordinate phosphorus are presented. The main types of radical reactions of phosphorus and their mechanisms are considered.
The bibliography includes 225 references.

CONTENTS

I.	Introduction	449
II.	Phosphinyl radicals	450
III.	Phosphonyl radicals	451
IV.	Phosphoranyl radicals	453
V.	σ-Radicals with the phosphorus atom in the α- and β-positions	458
VI.	Radical-cations derived from phosphorus compounds	458
VII.	Radical-anions derived from phosphorus compounds	460

I. INTRODUCTION

The autoxidation of white phosphorus, the process to which phosphorus owes its name, proceeds via a branched radical-chain mechanism[1]. The autoxidation of phosphine is also a radical-chain reaction[2]. Nevertheless free radicals derived from phosphorus compounds remained little studied for a long time, since in the first stages of the development of phosphorus chemistry investigators concentrated their attention on the study of heterolytic reactions. In 1945 Kharasch et al.[3] established that free radicals are involved in the reaction of PCl_3 with oct-1-ene; somewhat later a free-radical mechanism was proposed by Soborovskii et al.[4] for the joint oxidation of PCl_3 and hydrocarbons. At the beginning of the 1960s many reactions of phosphorus compounds were regarded as having a free-radical mechanism[5,6].

In 1961 Horsfield et al.[7] detected by ESR the $\dot{P}O_3^{2-}$ radical-ion on γ-irradiation of $Na_2HPO_3.5H_2O$ crystals. Subsequently numerous phosphorus-containing free radicals were detected by ESR and it was shown that their formation is indeed an intermediate stage in a number of reactions. At present the study of free radicals derived from phosphorus compounds and of their role in chemical reactions is being prosecuted vigorously and on a large scale.

Free radicals derived from phosphorus compounds can be divided into three groups: phosphinyl ($R_2\dot{P}$), phosphonyl ($R_2\dot{P}O$), and phosphoranyl ($R_4\dot{P}$). The aminyl and iminoxy- or nitroxy-radicals correspond to the first and second

groups respectively, while the third group has no analogues among nitrogen radicals. Furthermore, radical-cations derived from phosphines ($R_3P^{\cdot+}$) and their derivatives and also radical-anions containing tri- or tetra-coordinate phosphorus are known. The properties of the radical-anions of tri-coordinate phosphorus resemble those of phosphonyl radicals and those of tetra-coordinate phosphorus resemble the properties of phosphoranyl radicals.

II. PHOSPHINYL RADICALS

1. Generation

Phosphinyl radicals can be generated by the homolytic dissociation of the P–X bond on heating, irradiation, or abstraction of the substituent X by another radical. For example, $\dot{P}F_2$ radicals are generated on irradiation of ND_4PF_6 with γ-rays [8], on irradiation of PF_3 with electrons in a sulphur hexafluoride [9] or xenon hexafluoride (XeF_6) [10] matrix, on thermal dissociation of P_2F_4 and PF_2H [11,12] (they cannot be obtained on heating PF_3), and on ultraviolet irradiation of PF_2H in an argon matrix [12]. $\dot{P}Cl_2$ radicals were obtained by the ultraviolet irradiation of PCl_3 at −196°C [13], the condensation of PCl_3 or PBr_3 and lithium vapours in argon at −258°C yielded $\dot{P}Cl_2$ and $\dot{P}Br_2$ radicals [14], and $\dot{P}I_2$ radicals were produced by the photolysis of P_2I_4 and PI_3 in hexane or cyclohexane [15].

The simplest phosphinyl radical $\dot{P}H_2$ was identified by flash photolysis [16,17], $\dot{P}F_2$ was identified by mass spectrometry [18], and $\dot{P}Cl_2$ was identified by infrared spectroscopy [14]. All these radicals and many other phosphinyl radicals were also studied by ESR [8–10, 12, 19–22]; the parameters of their ESR spectra are presented in Table 1. Phosphinyl radicals with alkyl groups at the phosphorus atom have not so far been detected by any physical method.

2. Structure

The unpaired electron in the $\dot{P}H_2$ radical is in the p orbital of phosphorus at right angles to the plane of the bonds; the ground state [17] of the radical is $^2B_1$ and its electronic configuration is $KL\,(1a_1)^2\,(1b_2)^2\,(2a_1)^2\,(1b_1)^1$. The unpaired electron in $\dot{P}F_2$ is also in similar p orbitals of phosphorus and fluorine; these are typical π-electron radicals. According to the most reliable data [10], the values of a_P for both radicals are almost the same (Table 1). Therefore the delocalisation of the unpaired electron in $\dot{P}F_2$ should be small and the observed slight splitting by ^1H and ^{19}F nuclei is due to the σ–π interaction. $\dot{P}Cl_2$ radicals should have analogous properties. The ESR spectra of $\dot{P}Br_2$ and $\dot{P}I_2$ have not been studied.

The infrared spectra of $\dot{P}Cl_2$ and $\dot{P}Br_2$ have shown [14] that these radicals are non-linear; according to the calculation of the normal vibrations, the valence angle in both radicals is close to 120° and the force constants of the P–X bond are approximately the same as for PCl_3 and PBr_3 molecules. Thus in these cases too the stabilisation of the radical by the delocalisation of the unpaired electron over the halogen atom should be small.

Kilcast and Thomson [23] calculated the equilibrium geometry and the distribution of spin density in the simplest phosphorus radicals by the unrestricted Hartree–Fock method in terms of the CNDC/2 approximation; the valence angles and bond lengths were found by minimising the total energy. The results of the calculation on phosphinyl radicals are presented in Table 2. As was to be expected, the spin density in $\dot{P}F_2$ and $\dot{P}Cl_2$ is concentrated mainly in the phosphorus p orbital. Accordingly the electrons involved in the formation of bonds are appreciably displaced towards the ligand atoms; for example, the charges on the fluorine atoms are −0.26. Owing to the repulsion of these charges, the valence angle in $\dot{P}F_2$ is greater than in $\dot{P}H_2$. The bonds are elongated compared with the initial phosphines. Comparison of the calculation [23] with experimental ESR data showed that the values of a_P found previously [8,12] were erroneous. A non-empirical calculation on $\dot{P}F_2$ with inclusion of the 3s and 3p orbitals of fluorine and the 3d, 4s, and 4p orbitals of phosphorus in the basis set confirmed this conclusion [24]. The equilibrium geometry of $\dot{P}Cl_2$ calculated by Kilcast and Thomson [23] is not entirely reliable, since it does not apparently correspond to the true total energy minimum.

Table 1. Parameters of the ESR spectra of phosphinyl radicals.

Radical	g-Factor	Type of splitting	Isotropic splitting constants, G		References
			a_P	a_X	
$\dot{P}H_2$	2.0087	2×3	80	18	19
$\dot{P}F_2$	2.0108	2×3	36	60.5	8
	1.9952	2×3	47	65	12
	2.0020	2×3	84.6	32.6	10
$\dot{P}Cl_2$	2.014	2×7	71	5	13
$\dot{P}HPh$		2	251		20
$\dot{P}Ph_2$	2.0036	2×4	12.0	5.8	21
$\dot{P}(OEt)_2$	2.002	2	78.5		22

Table 2. The distribution of spin densities and equilibrium structures of phosphinyl radicals.

Radical	Spin density at the $3p_\pi$ atomic orbital of phosphorus	∠XPX	R_{PX}, Å
$\dot{P}H_2$	1.000	91.5° *	1.52
$\dot{P}F_2$	0.937	112°	1.73
$\dot{P}Cl_2$	0.718	140°	1.95

*Experiment [17]: ∠HPH = 91.7°, R_{PH} = 1.429 Å.

The $Ph\dot{P}H$ radical is distinguished by an exceptionally high constant a_P, but the reasons for this anomaly have not been elucidated. The lower value of a_P for $\dot{P}Ph_2$ is due to the delocalisation of the spin density over the radical. Wong and Wan [21] suggest that it is delocalised only over one benzene ring, where the protons in the *ortho*- and *para*-positions are equivalent; however, this interpretation of the observed spectrum is fairly controversial.

3. Reactions of Phosphinyl Radicals

All phosphinyl radicals, particularly those containing alkyl groups, are very unstable. Pellon [25], who determined the chain transfer rate constants for phosphinyl radicals in the polymerisation reactions of styrene and methyl methacrylate, established the following stability series for phosphinyl radicals: $Ph\dot{P}H > (NCCH_2CH_2)_2\dot{P} > C_8H_{17}\dot{P}H \simeq NCCH_2CH_2\dot{P}H$.

Two types of reactions are characteristic of phosphinyl radicals: (1) the abstraction of an atom from an adjacent neutral molecule; (2) addition to a double bond.

Reactions involving the abstraction of an atom (usually a hydrogen atom) normally take place when the radical interacts with the solvent, for example in the photolysis of triphenylphosphine in benzene in an atmosphere of nitrogen [26]:

$$Ph_3P \xrightarrow{h\nu} Ph_2\dot{P} + Ph^{\cdot} , \quad (1)$$

$$Ph_2\dot{P} + C_6H_6 \rightarrow Ph_2PH + Ph^{\cdot} . \quad (2)$$

Various mechanisms have been proposed for the reactions of $\dot{P}Ph_2$ with alcohols [26-28]. Wong et al. [29] established that they too involve the abstraction of a hydrogen atom from the α-carbon atom of the alcohol molecule (but not from the hydroxy-group, as shown in experiments with MeOD). Diphenylphosphine is partly oxidised to diphenylphosphine oxide. The data concerning the presence of alkyldiphenylphosphine [26] and phosphonium salts [27] in the reaction products were not confirmed [29].

Reactions involving the addition of phosphinyl radicals to double bonds are commonest and have been most thoroughly investigated. For example, $\dot{P}H_2$ reacts with olefins on ultraviolet irradiation or on heating to 80–100° of a mixture of PH_3, the olefin, and benzoyl peroxide [5]:

$$\dot{P}H_2 + R_2C{=}CH_2 \rightarrow H_2PCH_2\dot{C}R_2 . \quad (3)$$

The resulting radical reacts with another PH_3 molecule:

$$H_2PCH_2\dot{C}R_2 + PH_3 \rightarrow H_2PCH_2CHR_2 + \dot{P}H_2 . \quad (4)$$

The phosphine molecule can then give rise to the radical $H\dot{P}CH_2CHR_2$, which also adds to the olefin molecule; the reaction products are a mixture of primary, secondary, and tertiary phosphines. The addition reaction of phosphinyl radicals is reversible, since but-2-ene undergoes *cis–trans* isomerisation in the presence of $PhPH_2$, $n\text{-}Bu_2PH$, and $PH_2CH_2CH_2CN$, and azobisisobutyronitrile at 70°C. [30]

The reactions of PH_3, $PH_2CH_2CH_2CN$, and $PH(CH_2CH_2.CN)_2$ with cyclohexane [31], of phenylphosphine with allylamine, allyl acetate, and 2-methyl-5-vinylpyridine [32], and of PH_3 with fluoroolefins [33] proceed similarly, the phosphinyl radical always adding to the least substituted carbon atom. A kinetic study [34] of the reaction of tetrafluoroethylene with an excess of dimethylphosphine in the gas phase at 212–288°C showed that it is initiated by the bimolecular abstraction of a hydrogen atom from the dimethylphosphine molecule and proceeds subsequently via a free-radical chain mechanism in accordance with reactions (3) and (4); chain termination takes place as a result of the recombination of the dimethylphosphinyl radicals.

If the initial phosphine is unsaturated, the addition of phosphinyl radicals to a double bond can be modified; its products are telomers and polymers with phosphorus atoms in the chain. For example, phenylallylphosphine polymerises in this way on ultraviolet irradiation [5].

The mechanism of the reactions of PCl_3 with olefins should be analogous in principle [3]. In reality the yield of the products of the addition $\dot{P}Cl_2$ to olefins is low; high-boiling products are formed [35]. The reaction probably proceeds mainly via a different mechanism (see Section IV). The difference in the behaviour of $\dot{P}H_2$($\dot{P}Alk_2$, $Ar\dot{P}H$) and $\dot{P}Cl_2$ is probably due to the fact that the process involving the dissociation of the P–H bond and the addition of $\dot{P}H_2$ is exothermic (the dissociation of the P–H bond instead of C–H results in an energy gain of about 13 kcal $mole^{-1}$), while the corresponding reaction of PCl_3 is thermally neutral [5]. These considerations are confirmed by the absence of $\dot{P}F_2$ radicals in the thermolysis of PF_3. [12]

Phosphinyl radicals can also add to the C=N bond; the reaction of diethylphosphine and diphenylphosphine with isonitriles (in the presence of azobisisobutyronitrile as an initiator) is known [36]:

$$R_2\dot{P} + R'N{=}C \rightarrow R_2P\dot{C}{=}NR' \xrightarrow{} R_2PC{\equiv}N + \dot{R}' , \quad (5)$$

$$R_2\dot{P} + R'N{=}C \rightarrow R_2P\dot{C}{=}NR' \xrightarrow{R_2PH} R_2PCH{=}NR' + R_2\dot{P} . \quad (6)$$

Pathway (5) is preferred when R′ = CH_2PH or t-Bu and pathway (6) is preferred when R′ is another alkyl radical.

Finally, phosphinyl radicals can add to triple carbon–carbon bonds; for example, $PH_2CH_2CH_2CN$ and $PH(CH_2.CH_2CN)_2$ interact with hept-1-yne via a radical mechanism [32].

III. PHOSPHONYL RADICALS

1. Generation

The $(MeO)_2\dot{P}O$ and $(EtO)_2\dot{P}O$ radicals were detected by ESR on irradiation of single crystals of dimethyl and diethyl phosphites with X-rays [37]; in this case the main process is selective homolysis, so that only two types of radicals, uniformly distributed in the crystal, are formed. $(EtO)_2\dot{P}O$ can also be generated by the ultraviolet irradiation of triethyl phosphite at −196°C. Initially there is a homolytic dissociation of the O–C bond with formation of the $(EtO)_2\dot{P}O$ radical, which is then converted into $(EtO)_2PO$. [38]

Davies et al. [39] obtained $(RO)_2\dot{P}O$ radicals (R = Me, Et, i-Pr, or n-Bu) by the ultraviolet irradiation of solutions of the corresponding phosphites and di-t-butyl peroxide. When phosphites are treated with $TiCl_3 + H_2O_2$, products of the dissociation of the C–H bond in one of the alkyl groups are obtained instead of phosphinyl radicals. Thus the dissociation of the C–H bond is slower than the dissociation of the P–H bond.

The phosphinyl radicals $(MeO)_2\dot{P}O$ are also formed in the low temperature γ-irradiation of trimethyl phosphate [40], probably in consequence of the elimination of the MeO^- anion from the primary $(MeO)_3PO^{\cdot-}$ radical-anion (see Section VII). The $\dot{P}OCl_2$ radical was detected by ESR in γ-irradiated $POCl_3$ [41] and the $Ph_2\dot{P}O$ (Geoffroy and Lucken [42]) and $Me_2\dot{P}O$ (Begum and Symons [43]) radicals were detected in irradiated diphenylphosphinous acid and trimethylphosphine oxide respectively.

2. Structure

Table 3 lists the g-factors for phosphonyl radicals, the ^{31}P hyperfine splittings, and the spin densities ρ_S and ρ_p in the 3s and 3p orbitals of phosphorus. Evidently the latter are fairly large, so that the unpaired electron is not localised at the oxygen atom; this is confirmed by the difference between the ESR spectra of the $(EtO)_2\dot{P}O$ and $(EtO)_2\dot{P}O$ radicals [39]. With the exception of $Me_2\dot{P}O$ in the solid phase, splitting by protons is not observed, although the spin density in the $Ph_2\dot{P}O$ radical is undoubtedly delocalised over the benzene rings. The numerical values lead to the conclusion that the phosphonyl radicals are non-planar [37,42], but more accurate information about their structures is not available in the literature.

Chemical polarisation of ^{31}P nuclei was observed for the first time in the reaction of the t-BuO· and BzO· radicals with dialkyl phosphites [44]. This phenomenon was used as a method for the investigation of the generation and subsequent reactions of phosphonyl radicals derived from alkyl phosphites in the thermal decomposition of dicyclohexyl peroxydicarbonate (DCP) and dilauryl peroxide (DLP) [45-48], in the thermal decomposition of di-t-butyl peroxide [45,47], and in the ultraviolet photolysis of aldehydes and ketones [44,46] or phenylazotriphenylmethane [47]. Phosphonyl radicals are formed in all these reactions as a result of the abstraction of a hydrogen atom from the phosphite molecule; the hypothesis of the "adhesion" of the radicals derived from DCP and DLP to P=O bonds and the formation of radicals of the type $(RO)Ph(OMe)_2O$, put forward by Pobedimskii et al. [46], was disproved by Levin et al. [47] In the ultraviolet photolysis of phenylazotriphenylmethane phosphonyl radicals recombine with phenyl and triphenylmethyl radicals into singlet radical pairs with formation of phosphonates [47]; other reactions proceed similarly [45,47]. Chemical polarisation of ^{31}P nuclei in the reaction products of phosphonyl radicals released from cages was observed in the thermal decomposition of benzoyl peroxide in the presence of 2,2,6,6-tetramethylpiperidine *N*-oxide or toluene [45]. The reaction of dimethyl phosphite with peroxides is of quasifirst order; the activation energies for the reactions with DCP and DLP are 29.5 and 33 kcal mole^{-1} respectively [48].

Table 3. Parameters of the ESR spectra of phosphonyl radicals.

Radical	g-Factor	$a_{iso}(^{31}P)$, G	ρ_s	ρ_p/ρ_s	References
$(MeO)_2\dot{P}O$		684	0.188	2.86	37
	2.004	700	0.192		39
	2.005	691	0.190		40
$(EtO)_2\dot{P}O$		671	0.184	2.98	37
	2.032	762	0.209		38
	2.005	687	0.189		39
$(EtO)_2P'O'$	2.021	445	0.122		38
$(i\text{-}PrO)_2\dot{P}O$	2.004	685	0.188		39
$(n\text{-}BuO)_2\dot{P}O$	2.005	688	0.189		39
$Cl_2\dot{P}O$	2.002	759*	0.209	1.6	41
$Ph_2\dot{P}O$	2.0036	390	0.107	5.6	42
$Me_2\dot{P}O$	2.005	375**	0.103	7.6	43

*$a_{iso}(^{35}Cl) = 18$ G.
**at −196°C; $a_H = 19$ G.

Phosphonyl radicals are relatively stable between −50° and −10°C. The reaction involving the abstraction of an atom from neighbouring molecules is apparently more characteristic of these species than of phosphinyl radicals. For example, at −28° they readily abstract the bromine atom from EtBr, t-BuBr, $PhCH_2Br$, and $CH_2=CHCH_2Br$, without adding to the double bond in the last case; the abstraction of a Cl atom proceeds with greater difficulty and is observed only for t-BuCl. In all cases the abstraction of a halogen was confirmed by ESR spectroscopy of the corresponding alkyl radicals [39]. Phosphonyl radicals can also abstract a hydrogen atom from the molecule of the initial phosphite, initiating a radical-chain reaction, but this process is slower than the abstraction of a bromine atom.

Phosphonyl radicals add to olefins in a manner resembling the addition of phosphinyl radicals [49,50]:

$$(RO)_2P(O)H + \dot{R}'' \rightarrow (RO)_2\dot{P}O + R''H \quad , \qquad (7a)$$

$$(RO)_2\dot{P}O + R'CH{=}CH_2 \rightarrow (RO)_2P(O)CH_2\dot{C}HR' \quad , \qquad (7b)$$

$$(RO)_2P(O)CH_2\dot{C}HR' + (RO)_2P(O)H \rightarrow (RO)_2P(O)CH_2CH_2R' + (RO)_2\dot{P}O. \qquad (7c)$$

The reactions proceed at 100–110°C in 55–75% yields [5]. The addition of phosphonyl radicals to acetylenes [51] and unsaturated silanes [52] has been described. The polymerisation of the monobutyl ester of vinylphosphinous acid also proceeds with participation of phosphonyl radicals, since it is initiated by azobisisobutyronitrile or heat and the infrared spectra indicate a heterochain structure of the phosphorocarbon polymer [53]. The process probably proceeds mainly via a polyaddition reaction.

The reduction of aryldiazonium salts by hypophosphorous acid to aromatic hydrocarbons takes place via a radical-chain mechanism [54]. In the chain initiation stage the hydrogen in the P–H bond adds to the aryl residue [55]; the resulting $H_2\dot{P}O_2$ radicals are probably of the phosphonyl type. Gragerov and coworkers [56] established that the initiation process is of second order with respect to the acid; during the process, chemical polarisation of phenyl protons is observed, probably in the singlet radical pairs $\overline{PhN_2 \cdot H_2PO_2}$.

In contrast to phosphinyl radicals, phosphonyl radicals do not abstract a hydrogen atom from an aromatic ring but add to it. Thus the $(EtO)_2\dot{P}O$ radicals, generated on heating diethyl phosphonate with di-t-butyl peroxide, add to the *para*-position of methyl benzoate with a yield of 65% [5], to the 9-position of anthracene and phenanthrene, to naphthalene and carbazole with formation of a mixture of isomers, and to dibenzofuran [57]. There is no reaction with pyridine and ferrocene.

Arbuzov and Kataeva [58] demonstrated by ESR the formation of triphenylmethyl radicals in the reaction of bromotriphenylmethane with $NaOP(OEt)_2$. Triarylchloromethanes also give rise to free radicals in this reaction [59]. Evidently phosphonyl radicals are formed together with these species, but cannot be detected owing to their rapid recombination.

Levin and coworkers [45,47] investigated the recombination reaction of phosphonyl radicals by the method based on the chemical polarisation of ^{31}P nuclei. The recombination products are the subphosphates $(RO)_2POP(O)(OR)_2$ and the hypophosphates $(RO)_2\overset{\overset{O}{\|}}{P} - \overset{\overset{O}{\|}}{P}(OR)_2$; chemical polarisation of ^{31}P nuclei is observed in both and the multiplet effect (E/A) was noted for tetracoordinate phosphorus. Consequently phosphonyl radicals are ambident: they can recombine both via phosphorus and via oxygen. This conclusion has been confirmed by the isomerisation of hypophosphates to subphosphates at 180°C. [60] Phosphonyl radicals recombine in singlet radical pairs.

The interaction of fluorenylidenetriphenylphosphorane with sodium results in the elimination of phenylsodium and the formation of a radical (I); the reaction of triphenylphosphazophenyl with sodium probably gives rise to the radical $Ph_2\dot{P}{=}NPh$ via the same mechanism [61]. Both radicals are formal analogues of phosphinyl radicals with a P=C or P=N bond instead of P=O.

IV. PHOSPHORANYL RADICALS

1. Generation

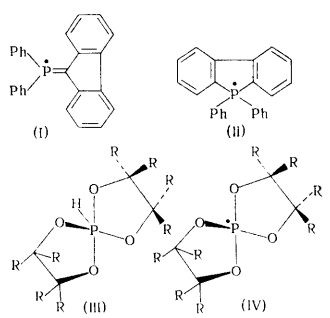
There exist three main methods for the generation of phosphoranyl radicals: the dissociation of the P–X bond in compounds of pentacovalent phosphorus; the one-electron reduction of phosphonium salts, and the addition of radicals to compounds of tervalent phosphorus.

Pentaphenylphosphorane can dissociate into the $\dot{P}Ph_4$ and $\dot{P}h$ radicals [62]. Razuvaev and Osanova [63] established that in chloroform and carbon tetrachloride the reaction products are PPh_4Cl and benzene, while in pyridine the product is phenyldiphenylenephosphine. Razuvaev et al.[64] showed with the aid of a deuterium label that the phenyl group is displaced from the axial and equatorial positions of the PPh_5 molecule with equal ease. In a study of the decomposition of $Ph_4P^{14}C_6H_5$ and $Ph_4PC_6D_5$ in benzene and of pentaphenylphosphorane in hexadeuteriobenzene the same workers [65] established that $\dot{P}Ph_4$ is formed preferentially "in the cage": the fraction of free radicals released into space is 5–6%. The rate of their release, determined [66] by fixation with diphenylpicrylhydrazyl and diphenylpicrylhydrazine, is 2.4×10^{12} species s^{-1} ml^{-1}.

The homolytic dissociation of the P–F bond is not characteristic of phosphorus pentafluoride and its derivatives. The reports [67,68] of the generation of $\dot{P}F_4$ on γ-irradiation of NH_4PF_6 crystals or KPF_6 powders are erroneous (see Section VII). The formation of the $\dot{P}Cl_4$ radical on dissociation of a P–Cl bond in the PCl_5 molecule has not been observed directly, but the reactions of PCl_5 with olefins and alkanes [69] proceed via this stage; the phosphorane $Cl_4PCH_2CH_2R$ is the product in the first case, while PCl_3, HCl, and an alkyl choride are produced in the second.

Bis-(2,2′-biphenylene)phosphorane decomposes in benzene at room temperature with formation of the phosphoranyl radical (II) [70], in which the unpaired electron is apparently delocalised over the π-electron system (a_P = 17.9 G). When spirophosphoranes (III) are acted upon by t-butoxy-radicals, the spirophosphoranyl radicals (IV) are formed [71,72] (see Scheme A).

Scheme A



Cathodic reduction of phosphonium salts leads to the formation of phosphoranyl radicals, which decompose with elimination of one of the ligands and retention of the configuration [73]. The rate of elimination of the ligand decreases in the sequence diphenylmethyl > benzyl > cinnamyl > hydroxymethyl > allyl > β-hydroxyethyl > t-butyl > isopropyl > n-butyl > ethyl > phenyl > methyl. The one-electron mechanism of the reduction of phosphonium salts with formation of phosphoranyl radicals has been confirmed by a polarographic method [74].

Nesmeyanov and coworkers [75] established that the one-electron reduction of tetraphenylphosphonium bromide to the $\dot{P}Ph_4$ radical can occur when the bromide is treated with lithium alkyls; the formation of radicals was confirmed by ESR. The subsequent reaction of the $\dot{P}Ph_4$ radicals depends on the type of electron-donating ion; the reaction products may be triphenylphosphine, phenyldiphenylenephosphine, or even triphenylphosphazophenyl (in the reaction with lithium n-butylamide).

The formation of phosphoranyl radicals from phosphorus(III) compounds was postulated as early as the 1950s by Kamai and Kharrasova [76] for the reaction of mixed alkyl phosphites with carbon tetrachloride, by Ramirez and McKalvie [77] for the reaction of triphenylphosphine with bromoform on ultraviolet irradiation, and by Walling and coworkers [78–80] for the reactions of phosphites and tertiary phosphines with the RO· or RS· radicals. The last two types of reactions have been reviewed [81]. Walling and Rabinowitz [79] proposed the following mechanism for the reaction of trialkyl phosphites with di-t-butyl peroxide:

$$t\text{-}Bu_2O_2 \rightarrow 2\dot{O}Bu\text{-}t \quad , \tag{8a}$$

$$(RO)_3P + \dot{O}Bu\text{-}t \rightarrow (RO)_3\dot{P}OBu\text{-}t \quad , \tag{8b}$$

$$(RO)_3\dot{P}OBu\text{-}t \rightarrow (RO)_3PO + t\text{-}Bu^{\cdot} \quad . \tag{8c}$$

Stage (8c) has been called β-decomposition. Triphenylphosphine interacts with t-butoxy-radicals via the same mechanism [80]. However, in the reaction of tributylphosphine with di-t-butyl peroxide 80% of the reaction product consists of dibutyl t-butylphosphinate and only 20% of tributylphosphine oxide [82]. Thus another pathway is possible in the transformation of phosphoranyl radicals – α-decomposition:

$$R_3\dot{P}OBu\text{-}t \rightarrow R_2POBu\text{-}t + R^{\cdot} \quad . \tag{9}$$

The formation of discrete phosphoranyl radicals via mechanism (8b) was confirmed by different methods. Bentrude and Wielesek [83] showed using a ^{14}C label that this process is irreversible and in addition stereospecific [84]. Levin and coworkers [45,85,86] observed negative chemical polarisation of the ^{31}P nuclei of tributyl and triphenyl phosphates in the reactions of the corresponding phosphites with t-butoxy-radicals, which demonstrated unambiguously the formation of phosphates from singlet radical pairs incorporating phosphoranyl radicals. Negative chemical polarisation of the ^{31}P nuclei of both possible decomposition products of phosphoranyl radicals—$CCl_3P(O)(OEt)_2$ and $BrP(O)(OEt)_2$—and also of triethyl phosphite, in conformity with the possiblity of α-decomposition, has been observed in the photolysis of the triethyl phosphite–bromotrichloromethane system [86].

Finally, phosphoranyl radicals obtained from phosphorus(III) compounds have been detected directly by ESR. Following the irradiation of PF_3, PCl_3, $MePCl_2$, Me_2PCl, and PH_3 in solid matrices, the ESR spectra of $\dot{P}F_4$ [9,10], $\dot{P}Cl_4$ [13], Me_nPCl_{4-n} (n = 1 or 2) [13], and $\dot{P}H_4$ [87] in solid matrices were observed. Kochi and Krusic [89–91] identified phosphoranyl radicals by ESR in the low-temperature photolysis of t-butyl peroxide in the presence of phosphine and mono-, di- and tri-methylphosphines and established that they are rapidly converted into secondary radicals containing two t-butoxy-groups and stable in the course of several minutes.

The stability of primary phosphoranyl radicals is appreciably influenced by the extent to which the phosphorus atom is sterically hindered. For example, the reaction of t-butoxy-radicals with trimethylphosphine results in the formation of the phosphoranyl and methyl radicals (α-decomposition), while only the ethyl radical is formed in the reaction with triethylphosphine [22,91].

Davies et al. [92-94] recorded the ESR spectra of a large number of radicals obtained from trialkyl phosphites via mechanism (8a)–(8b). The formation of phosphoranyl radicals has been confirmed by ESR in the reaction of t-butoxy-radicals with PEt_3, Et_2POEt, and $EtP(OEt)_2$, [95] with *NN*-dimethylamides of phosphorus(III) acids [96,97], and with chlorophosphines and phosphorochloridites [98]. According to the results of Davies et al. [93], methyl and n-butyl radicals do not react with trialkyl phosphites; the ESR spectra of the radicals $(RO)_2(R'O)\dot{P}Me$ were observed in a study [94] of the decomposition of azomethane in the presence of alkyl phosphites at −70°C, but their formation is probably reversible.

Table 4. Parameters of the ESR spectra of $\dot{P}X_4$, $\dot{P}X_3OR$, and $\dot{P}X_2(OR)_2$ radicals.

Radical	g-Factor	Isotropic splitting constants, G			Refs.
		a_P	a_{X_a}	a_{X_e}	
$\dot{P}F_4$	2.0033	1330	282	59 (2F)	9
		1391	360	⩽45 (2F)	10
$\dot{P}O_2F_2$	2.0100	93.8	52.5	—	88
$\dot{P}O_2Cl_2$	2.017	44	4.5	—	41
$\dot{P}H_4$	2.002	973.8	21	21	87
$\dot{P}Cl_4$	2.013	1214	62	7 (2Cl)	13
$MeP\dot{C}l_3$	2.000	1077			13
$(t\text{-BuO})Et\dot{P}OCl_2$	2.011	1145	34.1		98
$(t\text{-BuO})Me\dot{P}Cl_2$	2.010	1023	30.9		98
$(t\text{-BuO})Et\dot{P}Cl_2$	2.010	1003	31.3		98
$(t\text{-BuO})Et_2\dot{P}Cl$	2.008	794	38.9		98
$Me_3\dot{P}OH$	2.009	611.3			40
$(t\text{-BuO})\dot{P}H_3$		626.7	139.6	10.8 (2H)	91
$(t\text{-BuO})\dot{P}H_2Me$		631.5	139.6	9.76 (H)	91
				4.05 (3H)	
$(t\text{-BuO})\dot{P}HMe_2$		631.4	142.6	3.45 (6H)	91
$(t\text{-BuO})\dot{P}Me_3$		618.7	4.6	2.8 (6H)	91
$(t\text{-BuO})_2\dot{P}H_2$		672.5	—	0.6	91
$(t\text{-BuO})_2\dot{P}HMe$		703.3	—	6.84 (H)	91
				3.15 (3H)	
$(t\text{-BuO}_2\dot{P}Me_2$		713.7*		2.5 (6H)	91
		712.4**		2.3 (4H)	91
$(t\text{-BuO})_2\dot{P}Et_2$		713.9		2.3 (4H)	91
		705		2.3 (4H)	95
$i\text{-Pr}_2\dot{P}(OBu\text{-}t)_2$		714.6		1.7 (2H)	91
$Et_2\dot{P}(OBu\text{-}t)_2$		707		2.3 (4H)	95

*From Me_2Ph.
**From Me_3P.

2. Structure

The parameters of the ESR spectra of phosphoranyl radicals are listed in Tables 4 and 5. The hyperfine splittings by the two pairs of ^{19}F nuclei are different in the ESR spectra of $\dot{P}F_4$. [9,10] Consequently $\dot{P}F_4$ must be a structural analogue of the phosphorane PF_4H [99] and must have the structure of a trigonal bipyramid with two fluorine atoms in the axial positions and two in the equatorial positions; the *s* orbital of phosphorus contributes appreciably to the unpaired electron orbital, like the σ orbital of the P–H bond in phosphorane. This model has been confirmed by the observed [100] linear correlation between the a_P constants for $\dot{P}F_4$ and spirophosphoranyl and phosphonyl radicals on the one hand and the spin–spin interaction constants $^1J_{PH}$ for the NMR spectra of the corresponding phosphoranes on the other:

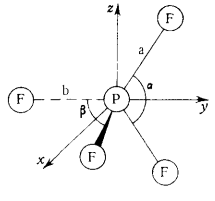
$$a_P = 1.52\,{}^1J_{PH} - 350\ .$$

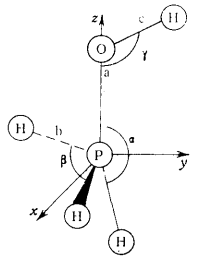
Table 5. Parameters of the ESR spectra of $(R'O)_2(R''O)\dot{P}R$ radicals [94,98].

R	R′	R″	Solvent	g-Factor	a_P, G
Me	Me	Me	Cyclopentane	2.003	783.1
			Hexane	2.003	784.3
Me	Et	Et	Cyclopentane	2.004	786.7
Me	i-Pr	i-Pr	Cyclopentane	2.004	787.4
Me	n-Bu	n-Bu	Cyclopentane	2.004	789.2
Me	t-Bu	t-Bu	Hexane	2.004	884.0
Me	Neopentyl	Neopentyl	Hexane	2.003	803.1
Me	cyclo-C_5H_9	cyclo-C_5H_9	Hexane	2.004	795.8
Me	Me	cyclo-C_5H_9	Hexane	2.003	785.3
Me	Et	cyclo-C_5H_9	Hexane	2.003	789.9
Me	Et	Benzyl	Hexane	2.003	791.2
Cl	Et	t-Bu	Cyclopentane	2.009	1037
Cl	$(CH_2)_2$	t-Bu	Cyclopropane	2.010	1034
Cl	$(CH_2)_3$	t-Bu	Cyclopropane	2.010	1033

Higuchi [101] carried out a quantum-chemical calculation on $\dot{P}F_4$ by the valence bond method and the molecular orbital method in Hoffmann's approximation: comparison of the structural parameters and the calculated spin densities shows that the valence angles in $\dot{P}F_4$ are virtually identical with those in PF_4H. The interatomic distances and the valence angles of $\dot{P}F_4$ have been optimised [23,102] within the framework of the unrestricted Hartree–Fock method (the CNDO/2 approximation) and it has been established that the trigonal bipyramidal structure of $\dot{P}F_4$ is somewhat distorted (Scheme B, Table 6) owing to the marked repulsion of the charges of the fluorine atoms.

Scheme B



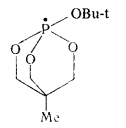


Calculation shows that the unpaired electron orbital of $\dot{P}F_4$ consists largely of the *s* orbital of phosphorus and the p_Z orbitals of the axial fluorine atoms; the d_{Z^2} orbital

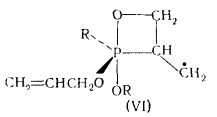
of phosphorus makes a contribution. The calculated *s*-orbital spin density of the phosphorus atom is therefore very large and agrees well with experiment[9,10]. However, the difference between the *s* spin densities at the axial and equatorial fluorine atoms is found to be much lower than follows from ESR data[9,10]; the total spin projection does not eliminate this discrepancy[102]. The higher constants for the splitting by the axial ^{19}F can probably be accounted for by the spin polarisation owing to the high spin density at the $2p_z$ orbitals.

The ESR spectra of $H_3\dot{P}OBu\text{-}t$, $Me\dot{P}H_2OBu\text{-}t$, and $Me_3\dot{P}OBu\text{-}t$ also showed that the ligands are non-equivalent[91], so that these radicals too must have the structure of a trigonal bipyramid close to that of the corresponding phosphoranes. The t-butoxy-group must occupy an axial position and the methyl group in $Me\dot{P}H_2OBu\text{-}t$ must be in an equatorial position according to the Muetterties rule[103]. The hyperfine splitting constant a_P for these radicals is smaller by a factor of two than for $\dot{P}F_4$, which indicates a decrease of the amount of *s* character of the unpaired electron orbital. This phenomenon was initially attributed to the distortion of the trigonal bipyramidal structure of the radicals owing to the decrease of the electronegativity of the ligands[92-94]. However, even a not unduly rigorous calculation on $H_3\dot{P}OMe$ by the CNDO/2 method[104] leads to the conclusion that the equilibrium structure of this radical is very close to that of a trigonal bipyramid. A recent calculation[102] of the optimal geometrical structures of the radicals $\dot{P}H_3OH$ and $\dot{P}H_2(OH)_2$ by the unrestricted Hartree–Fock method in terms of the CNDO/2 approximation showed that this conclusion[92-94] is erroneous: in both radicals the angle between the axial ligands is close to 180° (see Table 6). The calculated spin densities at the axial and equatorial hydrogen atoms in $\dot{P}H_3OH$ are very different, in contrast to the calculation on $\dot{P}F_4$; the use of spin projection yields values very close to the experimental results for $PH_3OBu\text{-}t$.

Scheme C



(V)



(VI)

R = t-BuO, EtO, or Me

R′=CH_2=$CHCH_2$.

According to a calculation[87], the $\dot{P}H_4$ structure is also close to that of an undistorted trigonal bipyramid; the equivalence of the hydrogen atoms observed in the ESR spectrum of $\dot{P}H_4$ has been explained by the fact that the energy barrier to the transition to the configuration with C_{3v} symmetry is very low—about 6 kcal mole^{-1}.

In the light of these data the hypothesis of a tetrahedral structure of the $\dot{P}Ph_4$ radical put forward by Razuvaev et al. [64] will be valid only subject to the condition that the interaction of the phosphorus atom with the benzene rings can alter significantly the geometrical structure of the phosphoranyl radical. This possibility has not been ruled out; Buck and coworkers[105] observed that a_P = 9.7 G (lower by two orders of magnitude than the usual value, see Tables 4 and 5) for the ESR spectrum of the $Ph\dot{P}(OMe)_2OBu\text{-}t$ radical obtained in the low-temperature interaction of dimethyl phenylphosphonate with t-butoxy-radicals and explained this finding by the transition of the radical to a tetrahedral configuration with almost the entire spin density concentrated in the benzene ring. Davies et al. [106] confirmed this result in a study of the ESR spectrum of the $C_6D_5\dot{P}(OMe)_2OBu\text{-}t$ radical; the a_P constants for the $Ph_2POEtOBu\text{-}t$ and $Ph_3POBu\text{-}t$ radicals are also reduced (23.0 and 45.0 G respectively). However, for very electronegative substituents at the phosphorus atoms, the constant a_P for phenylphosphoranyl radicals increases to a value characteristic of the trigonal bipyramidal configuration: for example, a_P = 1009 G for the ESR spectrum of $PhPCl_2OBu\text{-}t$. This spectrum shows a splitting due to the two equivalent ^{35}Cl (and ^{37}Cl) nuclei, which are evidently in the axial positions.

Table 6. Geometry of phosphoranyl radicals according to quantum-chemical calculations.

Radical	Valence angles, deg			Intraatomic distances, Å			Refs.
	α	β	γ	*a*	*b*	*c*	
$\dot{P}H_4$	162	97	—	1.42*	1.42*	—	87
$\dot{P}F_4$	174±5	109±9	—	—	—	—	101
	140	106	—	1.73*	1.73*	—	23
	140.6	105.6	—	1.727	1.722	—	102
$\dot{P}Cl_4$**	180	104	—	1.95	1.95	—	23
$\dot{P}H_3OH$	173.5	98	104.4	1.552 (P—H) 1.730 (P—O)	1.519	1.032	102
$\dot{P}H_2(OH)_2$	174.1	103.1	131.4	1.730	1.532	1.035	102
$\dot{P}H_3O^-$	178.5	95	—	1.565 (P—H) 1.760 (P—O)	1.542	—	102

*Assumed.

**Local minimum; errors in minimisation.

It follows from the ESR data[98] that the chlorine atom in the $(t\text{-}BuO)\dot{P}(OEt)_2Cl$ radical is in the axial position, i.e. is more apicophilic than the alkoxy-groups; this can also be accounted for by the electronegativity factor and by the weaker p_π–d_π P–Cl interaction†.

For the ESR spectra of the $(RO)_4\dot{P}$ radicals, where R is an alkyl substituent, we have g = 2.003–2.004 and a_P = 897 ± 11 G [93,94,107]; for the spirophosphoranyl radicals (IV) at −70°C, a_P = 910 G [71,72]. The constant a_P increases with the electronegativity of R also in bicyclic phosphoranyl radicals; thus a_P = 954.4 G for $(CF_3CH_2O)_2$.(EtO)(t-BuO)$\dot{P}$ [94] and 973.2 G for the radical (V) [93]. The constants a_P for the $(R'O)_2(R''O)R\dot{P}$ radicals, where R′ and R″ are alkyl groups, are also very close (Table 5); the $(t\text{-}BuO)_3\dot{P}Me$ radical is an exception, but these results are probably inaccurate. With decrease of the electronegativity of the ligands, a_P falls and proves to be

†The hydrogen atom in the $\dot{P}H(OMe)_3$ and $\dot{P}H(OH)(OMe)_2$ radicals is in the axial position[213,214], which is consistent with the Muetterties rules[103] when account is taken of the marked apicophilic properties of H.

anomolously high only for $\dot{P}H_4$. It has therefore been suggested that McDowell et al. [87] did not obtain the $\dot{P}H_4$ radicals but some other paramagnetic species [40,98].

3. Reactions of Phosphoranyl Radicals

It is evident from the literature data [80,82] that phosphoranyl radicals are capable of two types of reactions—β-decomposition via mechanism (8c) and α-decomposition, for example:

$$R_3\dot{P}OBu\text{-}t \rightarrow R_2POBu\text{-}t + R^{\cdot}. \qquad (9)$$

These two pathways in the transformations of phosphoranyl radicals can be traced also in the study of Davies et al. [94] The primary radical, for example H_3POBu-t, decomposes via mechanism (9), after which a secondary radical is formed:

$$H_3POBu\text{-}t + \dot{O}Bu\text{-}t \rightarrow H_3\dot{P}(OBu\text{-}t)_2. \qquad (10)$$

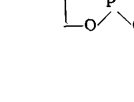
With increase of temperature, this radical probably decomposes via the β-mechanism:

$$H_3\dot{P}(OBu\text{-}t)_2 \rightarrow t\text{-}BuOP(O)H_2 + Bu\text{-}t. \qquad (11)$$

In the presence of an excess of t-butoxy-radicals the reaction can proceed further with formation of the t-BuOP.(O)R and $\dot{P}(BuO\text{-}t)_2$ radicals; one of them has been detected by ESR. [22]

Kinetic studies on the formation of phosphoranyl radicals via mechanism (8b) showed that this reaction is 500–1000 times faster than the abstraction of a hydrogen atom from solvent molecules [5]. The method of competitive reactions has been combined [92-94] with the recording of ESR spectra, which made it possible to determine the rate constants for the overall process $t\text{-}Bu\dot{O} + P(OR)_3 \rightarrow OP(OP)_3 + t\text{-}Bu$ and the β-decomposition of the phosphoranyl radicals [mechanism (8c)] and also the activation energies for these reactions. The kinetic parameters obtained are listed in Table 7. In agreement with the data of Bentrude and Wielesek [83], stage (8b) is irreversible and determines the rate of the entire reaction between the phosphite and the dialkyl peroxide, since the decomposition reaction (10) is slower than the β-decomposition and cannot compete with the latter [94]. The decomposition reaction of PR_3OBu-t and $\dot{P}R_3OBu\text{-}t)_2$ is of first order at 0°C and bimolecular at temperatures between −50° and −60°C. [21,98]

Table 7. Kinetic parameters of the β-decomposition of phorphoranyl radicals.

Radical	$k_{(-60^\circ)}$, s^{-1}	lg A	ΔH, kcal $mole^{-1}$
$(EtO)_4\dot{P}$	0.36	12.86	12.95
$(t\text{-}BuO)_4\dot{P}$	510		
$(t\text{-}BuO)\dot{P}(OEt)_3$	257	12.95	10.34
$(t\text{-}BuO)\dot{P}(OCH_2CF_3)$	4.5	8.25	7.4
	43.6		

The phosphoranyl radical in which one of the alkoxy-groups has been replaced by a chlorine atom shows a smaller tendency towards β-decomposition, which is believed to be due to the stabilisation of the ground state and the destabilisation of the transition state [98]. Phosphoranyl radicals in which phosphorus is incorporated in a five-membered ring exhibit an even greater resistance to β-decomposition. For example,  [94,98] does not split off the t-butyl group at 30°C. The spirophosphoranyl radicals (IV) are stable up to 120°C and their β-decomposition is so slow that there is sufficient time for the radicals to dimerise before this happens [71,72]. Both rings of (IV) are probably rigidly fixed. The unusual stability of the radicals (IV) enables them to add to hex-1-ene at −50°C, like phosphinyl radicals.

Phosphoranyl radicals containing prop-2-enoxy- or but-2-enoxy-groups at the phosphorus atom can cyclise with formation of the radicals (VI) in addition to undergoing β-decomposition [107]. The presence of t-butoxy-groups prevents the formation of the five-membered ring and the radicals derived from tri(pent-3-enyl) phosphite do not cyclise at all. a_P = 180 G and $a_{H_\alpha} = a_{H_\beta}$ = 20 G for the ESR spectra of the radicals (VI).

Davies and coworkers [93,94] explained the dual nature of the decomposition of phosphoranyl radicals on the basis of three factors: (1) the stereoselectivity of the decomposition; (2) the comparative stability of the secondary radicals; (3) pseudorotation. It is suggested that, in view of the appreciable weakness of the axial bonds, α-decomposition entails their dissociation while in β-decomposition the equatorial O–C bond is ruptured. It is then evident that the $Me_3\dot{P}OBu$-t radical will decompose via mechanism (10) only, in agreement with the data of Krusic et al. [91] It is also evident that the $R_2\dot{P}(OR)_2$ radical must be much more stable than $\dot{P}(OR)_4$, since the latter can undergo β-decomposition immediately. The $Et\dot{P}(OR)_3$ radical must be more stable than $Et_3\dot{P}OR$, since the dissociation of the P–O bond is more difficult than that of the P–C bond, in agreement with the results of Davies et al. [95]

Furthermore, the rate of β-decomposition is influenced by the nature of the radical removed: the lower its intrinsic stability the greater the difficulty of the β-decomposition and the more stable is the phosphoranyl radical. Consequently the rate constant for the decomposition of $\dot{P}(OBu\text{-}t)_4$ is higher by a factor of 1500 than that for the decomposition of $\dot{P}(OEt)_4$, while the $(PhO)_3\dot{P}OBu$-t radical cannot be detected by ESR at all [93]. In this case steric effects are unimportant, since the rate of decomposition of $\dot{P}(OBu\text{-}t)_4$ is only an order of magnitude higher than that for $t\text{-}BuO\dot{P}(OMe)_3$. [94]

Finally, in order to interpret the decomposition pathway of the phosphoranyl radical, one can employ the concept of pseudorotation proposed by Berry [103]. For example, the t-butoxy-group in the $\dot{P}(OMe)_3OBu$-t radical can enter the equatorial position by pseudorotation and subsequently, by virtue of the comparative stability of the secondary radicals, β-decomposition proceeds via this group [95]. In order to account for the decomposition of the $Et\dot{P}(OEt)_2(OBu\text{-}t)$ and $Et_2\dot{P}(OEt)(OBu\text{-}t)$ radicals with elimination of the ethyl radical [95], the decomposition of the $(t\text{-}BuO)_2\dot{P}(NMe_2)_2$ radical via the α-mechanism, and the characteristics of the reactions of t-butoxy-radicals with phosphoramidites containing five-membered rings, the concept of pseudorotation was also resorted to.

However, it is by no means universal. In the first place pseudorotation in phosphoranyl radicals is frequently inconvenient on energy grounds. Thus the activation energy for the reaction of triethylphosphine with t-butoxy-radicals via the α-mechanism is 1.34 kcal $mole^{-1}$, that for the α-decomposition of $Et_2\dot{P}(OEt)(OBu\text{-}t)$ is 8.16 kcal $mole^{-1}$ [95], while the energy of pseudorotation in $\dot{P}F_4$ has been estimated theoretically as 25 kcal $mole^{-1}$, the value for $\dot{P}H_3OH$ being higher still [102]. The broadening of the

components observed in the $\dot{P}H_3OBu$-t ESR spectrum above −70°C [104] is not due to pseudorotation but to the permutation of all the hydrogen atoms. The energy of this process in $\dot{P}H_3OH$ is 1.8–3.4 kcal mole^{-1} [102] and in $\dot{P}H_3OBu$-t the energy is 5.3 kcal mole^{-1} [104]. Even in those cases where pseudorotation in phosphoranyl radicals is possible, it evidently takes place slowly and at best can compete with bond dissociation.

Bentrude and Min [108] obtained evidence for the trigonal bipyramidal structure of phosphoranyl radicals and for the inadequacy of the concept of pseudorotation on the basis of chemical data. They investigated the reactions of phosphites with benzyl radicals via the mechanism

$$PhCH_2\dot{O} + (EtO)_2POR \rightarrow (PhCH_2O)\dot{P}(OR)(OEt)_2 \rightarrow \underset{41\%}{RO(OEt)_2PO} + \underset{49\%}{PhCH_2O(EtO)_2PO} \quad \begin{matrix}52\% \quad 44\% \\ (12a)\end{matrix}$$

$$R\dot{O} + (EtO)_2POCH_2Ph \quad (12b)$$

where R = $CH_2C_6H_4Me$-p; the numbers denote the yields of phosphine oxides in reactions (12a) and (12b) respectively. Evidently the alkoxy-groups in the intermediate phosphoranyl radicals are non-equivalent. The new substituent probably enters the axial position, in accordance with the Muetterties rule. If this factor is considered together with the yields of the products, it is found that the β-dissociation in the axial position is 1.3 times faster than in the equatorial position. In this case the pseudorotation factor is unimportant, since pseudorotation is slower than the β-decomposition. The attempt to account for the results [108] by competition between the β-dissociation processes in two axial positions is also invalid, since the introduction of a methyl group in the *para*-position of one of the aryl groups does not affect the ease of β-decomposition.

So far we have considered only the addition of fairly electrophilic radicals to phosphines and their derivatives. On this basis, it has been suggested [109] that a necessary condition for this reaction is a highly polar transition state. However, Davidson [110] established that diphenyl phosphonites react via the β-decomposition mechanism with methyl, isopropyl, and phenyl radicals; the reaction with t-butyl radicals is very slow and that with benzyl radicals does not occur. Fu and Bentrude [111] studied the kinetics of the reaction of trimethyl phosphite with phenyl radicals, which are intermediate between the alkoxy- and alkyl radicals both as regards electrophilic properties and the strength of the P–R bond. The formation of the phosphoranyl radicals $Ph\dot{P}(OMe)_3$ fully predominates in this reaction; next in importance is β-decomposition. The yield of the phosphonate is 99%, i.e. the phosphite absorbs all the kinetically free phenyl radicals. The interaction of methyl radicals with trimethyl phosphate is slower than that of phenyl radicals and triphenylmethyl radicals do not react with the phosphate at all. Fu et al. [112] determined the rate constant k for the molecular interaction of trimethyl phosphite with phenyl radicals ($k = 4.6 \times 10^6$ litre mole^{-1} s^{-1}) and estimated the activation energy for this process as 3.6 kcal mole^{-1}. The addition of phenyl radicals, like that of alkoxy-radicals, is irreversible: $BuOP(OMe)_2$ cannot be obtained from $PhP(OMe)_2$ and $\dot{O}Bu$. Fu et al. [112] suggest that the reaction of $\dot{P}h$ with the phosphite is exothermic; this should be even more true of the reactions of $R\dot{O}$ with phosphites.

Bentrude and coworkers [113–115] examined in detail the energetic aspect of the reactions of phosphorus(III) compounds with alkoxy-radicals. The decisive factor in these reactions is the thermodynamics of the formation of phosphoranyl radicals. The role of polar transition states may be neglected; for example, in the reaction of t-butoxy-radicals with the compounds $XC_6H_4P(OCH_3)_2$, where X = *p*-MeO, H, *p*-Cl, or *m*-CF_3, the polarity of the substituents hardly affects the rate of reaction [$k_{65°} = (3.1 - 3.7) \times 10^8$ litre mole^{-1} s^{-1} for X = H]. The formation of phosphoranyl radicals from the initial products is exothermic and their β-decomposition is more favourable on energy grounds than their α-decomposition owing to the stability of the P–O bond; this probably accounts also for the high reactivity of t-butoxy-radicals with respect to phosphorus(III) compounds. The heat of formation of the radical $\dot{P}X_3Z$ depends on the energy of the rehybridisation of the orbitals, bond energies, and the energy of resonance stabilisation. Thus the preferential occurrence of the α- or β-decomposition of $\dot{P}X_3Z$ is determined by the value of $\bar{D}_{PX_3}$, which is a measure of the P–X bond strength; when $\bar{D}_{PX_3} <$ 75 kcal mole^{-1}, the main reaction product is the phosphite or phosphonite. The formation of α- or β-decomposition products in the reaction with $PhCH_2\dot{O}$ radicals [108] has been explained by the weakening of the C–O bond and the decrease of the free energy of β-decomposition. As was to be expected, the probability of α-decomposition increases in the sequence X = Me < t-Bu < $PhCH_2$. Pseudorotation can be the rate-limiting stage of the process only in the α-decomposition of phosphoranyl radicals. Account must also be taken of the entropy effects.

4. Reactions Involving Phosphoranyl Radicals

Only the mechanisms of the reactions of $\dot{P}Ph_4$ and phosphoranyl radicals formed in the reactions with alkoxy- or phenyl radicals were examined previously. However the range of reactions involving phosphoranyl radicals is much wider. All the reactions involving the autoxidation of phosphines and phosphites have free-radical mechanisms. The oxidation of triethyl phosphite and secondary and tertiary phosphines by nitric oxide [5] and of triethyl phosphite by pyridine *N*-oxide [116], as well as other reactions proceed via the formation of phosphoranyl radicals with subsequent β-decomposition. It is usually believed [5,6] that the radical initiating the oxidation is initially converted into a peroxy-radical, this being followed by the formation of the phosphoranyl radical, whose decomposition initiates the chain:

$$\dot{R} + O_2 \rightarrow RO_2^{\cdot}, \quad (13a)$$

$$PEt_3 + RO_2^{\cdot} \rightarrow Et_3\dot{P}OOR, \quad (13b)$$

$$Et_3\dot{P}OOR \rightarrow Et_3PO + RO^{\cdot}, \quad (13c)$$

$$RO^{\cdot} + Et_3P \rightarrow Et_3\dot{P}OR. \quad (13d)$$

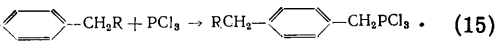
Ultimately $Et_2P(O)OEt$ and $EtP(O)(OEt)_2$ are also formed. Reaction (13b) is bimolecular; $k_{-95°} = 200$ litre mole^{-1} s^{-1} and $\Delta E = 3$ kcal mole^{-1} for PPh_3. [177] However, in these reactions oxygen can add directly to the phosphine or phosphite molecule; this process is possible for triphenyl phosphine and triethyl phosphite, while PCl_3 and $P(OBu\text{-}t)_3$ do not absorb oxygen without an initiator [117]. Phosphoranyl radicals can also combine with O_2; for example $(EtO)_4P\dot{O}O$ radicals ($g = 2.022$ and $a_P = 9.25$ G) and $(t\text{-}BuO)(EtO)_3P\dot{O}O$ radicals ($g = 2.021$ and $a_P = 9.45$ G) were detected [95] at −70°C in the presence of oxygen. Such radicals are stable at −50°C for a few minutes. When the entire oxygen has combined, only the ESR spectrum of the primary phosphoranyl radical is observed [118].

Peroxy-radicals are probably formed also in the oxidation of PCl_3. [4,119]. This reaction is self-initiated with formation of $\dot{P}Cl_2$ and $\dot{C}l$ and then proceeds via the mechanism

$$PCl_3 \xrightarrow{Cl} \dot{P}Cl_4 \xrightarrow{O_2} Cl_4POO^{\cdot} \xrightarrow{PCl_3} 2POCl_3 + Cl^{\cdot} \quad (14)$$

When a hydrocarbon is added to PCl_3 in the presence of O_2, the products are PCl_3 and $PCl_3O\dot{O}$ and ultimately $POCl_3$ and $RPOCl_2$; the compounds $RPCl_2$ were obtained at 575–600°C. [5]

It has already been mentioned (see Section II) that the role of phosphinyl radicals in the reaction of PCl_3 with olefins is insignificant. This reaction proceeds via the formation of the phosphoranyl radicals $Cl_3PCHR'\dot{C}H_2Cl$ by the addition of $\dot{C}l$ and PCl_3 to the olefin molecule [120]. The reaction of PCl_3 with *p*-xylylene proceeds via the same mechanism; a radical of the benzyl type is formed initially and then reacts with PCl_3 [5]:



(15)

The phosphoranyl radical adds to *p*-xylylene as a result of which poly-*p*-xylylene is formed even at −78°C.

The characteristics of the radical reactions of thiols and disulphides with phosphines and phosphites are the same as those of organic peroxides [5,78,112]. The reactivity of phosphorus compounds decreases in this case in the following sequence: $P(n\text{-}Bu)_3 > P(OEt)_3 > PPh_3 > P(OPh)_3$.

Phosphoranyl radicals may also be formed in the reaction of SCl_2, S_2Cl_2, $SOCl_2$, and SO_2Cl_2 with trialkyl phosphites. However, the radical mechanism of these reactions still has to be demonstrated [5].

Apart from the abstraction of a hydrogen atom and an alkyl group and the formation of the radicals discussed in Section V, the reactions of phosphoranyl compounds with phenyl radicals can entail the formation of phosphoranyl radicals by the addition of the phenyl radical to be phosphoranyl oxygen; however, they rapidly disproportionate [121].

V. σ-RADICALS WITH THE PHOSPHORUS ATOM IN THE α- AND β-POSITIONS

When phosphorus acid esters react with hydroxy-radicals in aqueous solutions (for example on treatment with Fenton's reagent), radicals of the type $(R'O)_2P(O)\dot{O}CHR$ or $R'(R'O)P(O)\dot{O}CHR$ (R = H, Me, or Et), which have been detected in a flow system by ESR, are formed [122,123]; the same radicals have been detected in other studies [124], [125] on low-temperature irradiation of trialkyl phosphates. Estimates of Q^{H}_{CH} for these radicals show that the phosphoryl group has a greater inductive and a weaker mesomeric effect than the acetyl group: a^P = 10–32 G [122,123]; thus the spin population of the 3*s* orbital of phosphorus $\rho_S(^{31}P)$ = 0.003–0.009. The overall spin density at phosphorus in $(R'O)R'P(O)\dot{O}CHR$ radicals is 0.08–0.09; splitting by phosphorus in $(R'O)R''\dot{P}(O)CH_2\dot{C}HR$ radicals has not been observed [123].

β-phosphoryl radicals formed via mechanism (7b) have been detected by ESR [38]. Their $\rho_S(^{31}P)$ is much lower than for phosphonyl radicals (about 0.03); $\rho_S(H)$ for the CH_2 group is of the same order of magnitude—lower than for Et and $(RO)_2P(O)\dot{O}CH_2$. [124] The decrease of spin density at the protons has been explained by the fact that the P–C bond screens the *p* orbital of the unpaired electron and rotation about the C–C bond in the $(RO)_2P\dot{O}CH_2.\dot{C}HR'$ radical is hindered.

These results are consistent with the general conclusion of Krusic and Kochi [126] that the conformation with the MR''_3 group displaced from the plane and the maximum overlapping of the electron cloud of the C–M bond and the *p* orbital of the unpaired electron is preferred for radicals of the type $R_2\dot{C}CR'_2MR''_3$ (M is an element in the Third or higher Period). This phenomenon can be explained satisfactorily by the delocalisation of the unpaired electron as a result of hyperconjugation [127]; then the splitting by the ^{31}P nucleus will be proportional to the spin density at the α-carbon atom and $\cos^2\theta$, where θ is the angle between the C–M bond and the axis of the unpaired electron orbital. Damerau et al. [128,129] obtained in aqueous solutions radicals of the type $(RO)_2P(O)CH.\dot{C}(OR')CCl_2$, which are characterised by a high value of a^P (60–69 G), very sensitive to changes in R and R′, in contrast to a_H; with increase of temperature, a^P decreases sharply in accordance with the hyperconjugation model. The authors [129] estimated θ = 57.2° from the value of a^P. For the radicals $(RO)_2P(O)C\dot{R}'OH$, [128] $a^P \simeq$ 30 G, is independent of temperature, and is probably due to spin polarisation [129].

On the basis of the *g*-factors for the $R_2\dot{C}CR'_2MR''_3$ radicals, Kawamura and Kochi [130] suggested that in these radicals there is a possibility of a direct delocalisation of the unpaired *p* electron over the *d* orbital of M. However, such delocalisation must be insignificant in principle [131]. In the case of phosphorus it does not occur at all, since *g* = 2.0027 for $(MeO)_2P(O)C(OH)Me\dot{C}H_2$ [128], and for $\dot{P}O_3^{2-}$ it is less than 2.002 (see Section VII, 1), while delocalisation over the *d* orbital should lead to a decrease of the *g*-factor.

Low-temperature irradiation of trialkylphosphines yielded radicals of the type $R_2P - \dot{C}R'_2$ [132]; the splitting by the ^{31}P nucleus in their ESR spectra was interpreted as a result of spin polarisation.

Arbuzov et al. [133] investigated the ESR spectra of the phosphonohydrazyl radicals $Ph_2N\dot{N}P(O)R_2$ (R = Ph, OPh, or OEt) in solution. The sum of the constants for the splitting by the two ^{14}N nuclei is lower than for diphenylpicrylhydrazyl; part of the spin density is probably delocalised over the phosphoryl group. A similar result was obtained from the ESR spectra of thiophosphonohydrazyl radicals [134].

VI. RADICAL-CATIONS DERIVED FROM PHOSPHORUS COMPOUNDS

1. Generation

The radical-cations $\dot{P}H_3^+$ [135], $Et_3P^{\dot{+}}$ [135], $Bu_3P^{\dot{+}}$ [135], and $Me_3P^{\dot{+}}$ [136] were obtained by the low-temperature γ-irradiation of phosphine and trialkylphosphines in sulphuric acid at −196°C; irradiation of a mixture of orthophosphoric and sulphuric acids gave $^{+}\dot{P}(OH)_3$ [137] and not the phosphoranyl radical $\dot{P}(OH)_4$. The dimeric radical-cations $(R_3P)_2^{\dot{+}}$ were detected after irradiation of pure trialkylphosphines [137,138].

Many reactions of phosphines may include a stage involving one-electron oxidation with formation of radical-cations. Ramirez and Dershowitz [139] reported the appearance of ESR signals in the reaction of triphenylphosphine with cloranil. However, these signals were not due to the radical-cations $Ph_2^{\dot{+}}$ but to products of their addition to the oxygen atom in the chloranil molecule [140,141]. The ESR signals in the reaction between triethylphosphite and chloranil have the same origin [141]. ESR signals were also recorded in the triphenylphosphine–sulphur [142], triphenyl-

phosphine–benzoquinone[143], and triphenylphosphine–2,5-dichlorobenzoquinone[144] systems. In the last two cases they are due to semiquinone radicals—derivatives of phosphobetaines; similar stable 4-R-2,6-di-t-butylphenoxy-radicals (R = PPh_2, $POPh_2$, $PSPh_2$, etc.) were also investigated[145].

The ESR spectra of the products of the addition of the corresponding radical-cations to 2-methyl-2-nitrosopropane were detected in the reaction of $P(OEt)_3$ and $P(NMe_2)_3$ with 9,10-phenanthrenequinone; in the presence of an excess of $P(NMe_2)_3$, the spectrum of the adduct of the dimeric radical-cation was observed[146].

The anodic oxidation of triphenylphosphine in methanol results in the formation of triphenylphosphine oxide[147], probably via the radical-cation stage. Triarylphosphines can also be converted into the radical-cations $Ar_3P^{\cdot+}$ and then into triarylphosphine oxides under the influence of tetracyanoethylene and tetracyano-*p*-quinodimethane.[148] Dimroth and coworkers[149-151] obtained radical-cations derived from 2,4,6-triphenylphosphabenzene (TPB) and its analogues with two and three C_6D_5 groups by oxidation with phenoxy-radicals, $Pb(OAc)_4$, $Pb(OBz)_4$, or $Hg(OAc)_2$. 1,1-Dimethoxy-, 1,1-diaryloxy-, and 1,1-diaryl-TPB are also readily oxidised to the radical cations[152-154].

Lucken and Mazeline[155] obtained the radical-cation $Ph_3\overset{+}{P}\dot{C}H_2$ by the low-temperature irradiation of triphenylmethylphosphonium chloride; Lyons and coworkers[132,140,156] obtained the radical-cations $R'_3\overset{+}{P}\dot{C}Me$ (R = H, Me, or COPh) in irradiated phosphonium salts‡. After treating aqueous solutions of phosphonium salts with Fenton's reagent, Lucken[157] recorded the ESR spectra of $(HOCH_2)_2\overset{+}{P}\dot{C}HOH$ and $(HOCH_2)_3\overset{+}{P}\dot{C}HOH$.

Buck and coworkers[158,159] generated the radical-cations $Ph_3\overset{+}{P}\dot{C}Ph_2$ and $Ph_3\overset{+}{P}\dot{C}(C_6H_4OMe\text{-}p)_2$ by the anodic oxidation of the corresponding ylides, by the cathodic reduction of the dications obtained by treating the ylides with $AgBF_4$, and by the reaction of the dications with the ylides.

2. Structure

The simplest radical-cation $PH_3^{\cdot+}$ is characterised by an appreciable isotropic interaction of the unpaired electron with the ^{31}P nucleus (Table 8).

According to the theory of the dependence of the valence angles φ in the AB_3 radicals on the nature of the A–B bond[127], the following relation holds between φ and the hybridisation parameter $\lambda = \sqrt{\rho_p/\rho_s}$:

$$\varphi = \arccos\left[\frac{1}{2}\left(\frac{3}{2\lambda^2+3}-1\right)\right] \qquad (16)$$

The use of Eqn. (16) yields $\varphi = 114°$ for $PH_3^{\cdot+}$. Boyd and Whitehead[160] found φ ranging from 112 to 120°, depending on the choice of parameters, when they optimised the $PH_3^{\cdot+}$ geometry by a modified CNDO/2 method. These estimates of φ are probably too high, since the possible involvement of 3*d* orbitals in the formation of bonds was ignored in deriving Eqn. (16) and in the calculations[160]. The inclusion of the 3*d* orbitals of phosphorus in the basis set reduces the total $PH_3^{\cdot+}$ energy and decreases the equilibrium value of φ, as shown by the non-empirical calculation of Aarons et al.[161]; however, the numerical values of φ obtained for $PH_3^{\cdot+}$ in their study are also not entirely reliable owing to the limited basis set employed and the fixed bond length R_{PH}. Gorlov et al.[162] carried out a similar optimisation of the interatomic distances and valence angles in $PH_3^{\cdot+}$ by the UHF – CNDO/2 method; according to their data, $\varphi = 109°27'$ and $R_{PH} = 1.523$ Å, the spin density of the phosphorus *s* orbital being 0.122 after spin projection and the barrier to the $PH_3^{\cdot+}$ inversion being about 15 kcal mole^{-1}. Although these results are not final either, there is no doubt that the $PH_3^{\cdot+}$ radical-cation is non-planar.

Table 8. ESR parameters of radical-cations derived from phosphorus compounds.

Radical	*g*-Factor	Isotropic splitting constants, G		ρ_s (^{31}P)	$\frac{\rho_p}{\rho_s}$ (^{31}P)	References
		$a_{^{31}P}$	$a_{^1H}$			
$PH_3^{\cdot+}$	2.007	517		0.142	6.46	135
$PMe_3^{\cdot+}$	2.016	400		0.110	8.70	136
$PEt_3^{\cdot+}$	2.007	384		0.106	9.29	135,137
$P(n\text{-}Bu)_3^{\cdot+}$	2.008	360		0.099	9.61	135
$P(OH)_3^{\cdot+}$		795		0.218	3.00	40
$(PEt_3)_2^{\cdot+}$		455		0.125	3.31	138
$[P(n\text{-}Bu)_3]_2^{\cdot+}$		462		0.127	3.36	138
$Ph_3\overset{+}{P}\dot{C}H_2$	2.0033	37.0	19.4	0.010		155
$Ph_3\overset{+}{P}\dot{C}MeCOOH$	2.0025	37.0	23.5	0.010		155
$Ph_3\overset{+}{P}\dot{C}Ph_2$		26.6	3.0 (*p*) 2.7 (*o*) 1.2 (*m*)	0.007		158

The valence angles in the radical-cations derived from alkylphosphines, found by Eqn. (16), are greater than for $PH_3^{\cdot+}$, although, according to Walsh's rules for the effect of the ligand electronegativities on the valence angles, their decrease was to be expected; the hyperconjugation of phosphorus with the alkyl groups probably has an effect here[135]. The dimeric radical-cations $(R_3P)_2^{\cdot+}$ have a more pyramidal structure than the monomeric radical-cations. Possibly the radical identified[87] as $\dot{P}H_4$ was in reality the dimeric radical-cation $P_2H_6^{\cdot+}$.

Powell and Hall[148] established that the reactions of optically active arylphosphines with tetracyanoethylene and with tetracyano-*p*-quinodimethane yield the racemic phosphine oxides; consequently the $PH_3P^{\cdot+}$ radical-cation must be planar or must be characterised by a very low inversion barrier. Since the $PH_3^{\cdot+}$ radical-cation is pyramidal, the flattening of the $Ph_3P^{\cdot+}$ structure must be due to the unusual nature of the interaction between the phenyl groups and the phosphorus atom.

A delocalisation of spin density due to the $p_\pi - d_\pi$ interaction is in principle possible in radical-cations where the phosphorus atom can form part of the *p*-electron system. It is observed, for example, in the TPB radical-cation[150-152]. The splitting constants are 22 – 27 G for the ^{31}P nucleus and 2.4 G in each case for the *meta*-protons of the TPB ring and the *ortho*- and *para*-protons of the benzene ring. In the radical-cations derived from 1,1-diaryloxy- and 1,1-diaryl-TPB the unpaired electron is not delocalised over the substituents at the phosphorus atom[152-154]: $a_P = 20$ G.

The rotation of the methylene group in $Ph_3\overset{+}{P}\dot{C}H_2$ is probably hindered[155], also in agreement with the concept of the $p_\pi - d_\pi$ interaction. However, the splitting by the ^{31}P nucleus in the ESR spectra of the radical-cations

‡Irradiation of $Ph_3\overset{+}{P}\bar{C}(Me)COOH$ gives rise to the ESR spectrum of the cyclohexadienyl radical with the phosphorus atom at the methylene carbon atom[215].

$R_3\dot{P}\dot{C}RMe$ [156], $(HOCH_2)_2\dot{P}H\dot{C}HOH$, and $(HOCH_2)_3\dot{P}\dot{C}HOH$ [157] was interpreted as a result of the spin polarisation of the P–C σ bond; the delocalisation of the spin density at the phosphorus atom due to the $p\pi-d\pi$ interaction is very slight according to some investigators [137, 156]. The same conclusion was reached in other studies [158, 159] on the basis of the ESR spectra of $Ph_3\dot{P}\dot{C}Ph_2$ and $Ph_3\dot{P}\dot{C}(C_6H_4.OMe\text{-}p)_2$. The distribution of spin density over the benzene rings and the carbon atom in these radical-cations and in the diphenylmethyl radical [163] is similar; consequently the phosphorus atom is not involved in conjugation and the splitting by its nucleus is due to spin polarisation.

The radical-cations derived from salts of 1,4-diphosphoniacyclohexa-2,5-diene, which are stable at 20°C, have been investigated [164]; $a_P \simeq 16$ G at −60°C and decreases with increase of temperature, possibly in consequence of a change in the conformation of the radical-cation, leading to a change in the hybridisation of the phosphorus atom.

VII. RADICAL-ANIONS DERIVED FROM PHOSPHORUS COMPOUNDS

1. TETRAATOMIC RADICAL-ANIONS

a. Generation

The first phosphorus-containing radical-anion identified by the ESR spectrum was $\dot{P}O_3^{2-}$ in γ-irradiated $Na_2HPO_3.5H_2O$ and $BaHPO_3.6H_2O$ crystals [7]. This radical-anion was also detected after irradiation with X-rays of crystalline magnesium, strontium, and cadmium phosphites [165], ammonium hydrogen phosphate [166], $(NH_4)_2P_2O_8$ [167], $(NH_4)_2PO_3F.H_2O$ [168], and $CaCO_3$ with an admixture of phosphite [169]; Schlick et al. [170] studied the ESR spectrum of $\dot{P}O_3^{2-}$ in irradiated $Na_2DP^{17}O_3.5D_2O$ crystals. Morton [171] recorded the ESR spectrum of the HPO_2^- radical-anion in a γ-irradiated ammonium hypophosphite single crystal and Atkins et al. [172] obtained this spectrum for irradiated crystals of sodium and magnesium hypophosphites. Fessenden [173] detected by ESR the FPO_2^- radical-ions in NH_4PF_6 and these were subsequently also found [174] on γ-irradiation of KPO_2F_2. The HPO_2^- and $\dot{P}O_3^{2-}$ radical-ions were obtained in aqueous solutions almost simultaneously by Beckwith [175] and by Norman and coworkers [176] by treating hypophosphorous and phosphorous acids with Fenton's reagent; the latter yields the HPO_3^- radical-ion in an acid medium [175]. Low-temperature irradiation of dimethyl and diethyl phosphites gave, apart from phosphonyl radicals, also the $MeOPO_2^-$ and $EtOPO_2^-$ radical-ions, while only the latter radicals were found in frozen solutions of phosphites in 2-methyltetrahydrofuran [37]. Irradiation of solid phenylphosphinic acid salts with X-rays [177] and their treatment with Fenton's reagent in aqueous solutions [176] yielded the $PhPO_2^-$ radical-anion, while the neutral $Ph\dot{P}(O)OH$ radical was obtained in irradiated phenylphosphinic acid powder [177].

b. Structure

The parameters of the ESR spectra of the simplest phosphorus-containing radical-anions are presented in Table 9. Judging from the values of ρ_P/ρ_S, these radical-anions must be non-planar [178], particularly if the contribution of the 3*d* orbitals of phosphorus to the formation of bonds is considerable (see Section VI). The numerical value of the valence angle in $\dot{P}O_3^{2-}$ depends on the nature of the matrix. With increase of the ρ_P/ρ_S ratio, the overall spin density at the phosphorus atom diminishes; in this respect the $\dot{P}O_3^{2-}$ radical-ion differs from NO_3^{2-}. [179]

A quantum-chemical calculation on $\dot{P}O_3^{2-}$ with a pyramidal structure [168] by the molecular orbital method in Hoffmann's approximation led to a satisfactory agreement between the calculated and experimental splitting constants. After optimising the $\dot{P}O_3^{2-}$ geometry by the unrestricted Hartree–Fock method in terms of the CNDO/2 approximation, Kilcast and Thomson [23] found that the energy minimum corresponds to a planar structure ($\varphi = 120°$, $R_{PO} = 1.69$ Å). According to their data [23], the HPO_2^- and FPO_2^- radical-ions are non-planar. All the calculated *s* spin densities are somewhat higher than the experimental values; it was noted that the *s* spin density at the phosphorus atom increases as the radical-ion becomes flattened, contrary to Walsh's rule [127].

Table 9. ESR parameters of phosphorus-containing radical-anions.

Radical	*g*-Factor	Isotropic splitting constants, G		ρ_s (^{31}P)	$\frac{\rho_p}{\rho_s}$ (^{31}P)	Refs.
		$a_{^{31}P}$	a_X			
$\dot{P}O_3^{2-}$	2.0003	594		0.163	3.21	7
	1.999	675		0.185	3.00	165
		627		0.172	3.16	166
	2.0008	751		0.206	2.65	167
		554		0.152	2.72	168
	2.0016	700		0.192	3.01	169
	2.0014	571		0.157		175
	2.0018	644		0.177		176
HPO_3^-	2.0020	658		0.181		175
HPO_2^-		495	82.5 (^{1}H)	0.136		171
	2.0028	484	90	0.133		175
	2.0028	478	89.5	0.131		176
$MeOPO_2^-$		556		0.153	2.94	37
$EtOPO_2^-$		557		0.153	2.99	37
FPO_2^-	2.001	699	169 (^{19}F)	0.192		173
$PhPO_2^-$	2.0001	468		0.129		176
	2.0030	490.5–514		0.135–0.141	4.17–4.35	177
$\dot{P}O_4^{2-}$	2.015	29		0.008		195
$\dot{P}O_4^{4-}$	2.0106	1156		0.318	1.74	196
$POCl_3^-$	2.018	1359	67 (2 ^{35}Cl) 15 (^{35}Cl)	0.373		41
		1371	40 (2 ^{35}Cl) 18 (^{35} Cl)	0.376		201
$(PhPOCl)_2^-$	2.009	1000	51 (2 ^{35}Cl)	0.275	2.67	216
$(PNCl_2)_3^-$		1290		0.354		224

The increase of A_{iso} (^{31}P) and the enhancement of the pyramidal structure of the radical-ion on passing from $\dot{P}O_3^{2-}$ to HPO_3^- has been explained by a decrease of the repulsion between the electronic charges as a result of protonation. However, the qualitative distribution of spin density is not altered either by protonation or by the addition of an alkyl group. The $PhPO_2^-$ radical-anion is undoubtedly non-planar, in contrast to the $PhNO_2^-$ radical-anion. The valence angles in $PhPO_2^-$ are unknown; the *s* spin density at the phosphorus atom increases on protonation of $PhPO_2^-$ and depends on the type of cation in the matrix [177]. As a result of both these effects, the $PhPO_2^-$ radical-anions resemble more closely $\dot{P}O_3^{2-}$ and other tetra-atomic radical-ions.

c. Reactions of XPO_2^- Radical-anions

It follows from the foregoing that the $\dot{P}O_3^{2-}$ and HPO_2^- radical-anions can be regarded as dealkylated phosphonyl radicals. Since the influence of the alkyl groups is relatively slight [37, 38], presumably the chemical properties of

these radical-anions will resemble those of phosphonyl radicals. Indeed they are capable of reducing alkyl bromides, alkyl iodides, bromo- and iodo-substituted carboxylic acids, and diacetyl to alkyl radicals and phenyldiazonium salts to phenyl radicals ($\dot{P}O_3^{2-}$ is the most effective reducing agent [175]) and can also add to the C=C double bond in maleic, acrylic, and methacrylic acids and their anions, and 1,1-dimethylethylene and to the C=N bonds in $CH_2{=}NO_2^-$ and oximes [175,176]. However, the addition proceeds with greater difficulty than that of the $\dot{O}H$ and $\dot{N}H_2$ radicals and only to a carbon atom not bound to a polar group. It follows from the analysis of the ESR spectra of the radical addition products that the spin density is delocalised over the phosphorus atom; free rotation about the P–C bond is hindered; according to Beckwith [175], this can be explained only by the interaction of the unpaired electron with the 3*d* orbitals of phosphorus. The reactions of $PhPO_2^-$ in solution are similar to those $\dot{P}O_3^{2-}$ and HPO_2^-.

When irradiated NaH_2PO_3 is dissolved in aqueous solution of t-butyl nitroxide, $\dot{P}O_3^{2-}$ adds to the nitrogen atom of the N=O bond [175]. A similar reaction takes place between nitrobenzene or *p*-nitrobenzoic acid and $\dot{P}O_3^{2-}$ or HPO_2^-. [176]

2. RADICAL-ANIONS DERIVED FROM PHOSPHINES

The unpaired electron in the radical-anion derived from a phosphorus(III) compound can be stabilised by delocalisation of the π-electron system and can occupy the lowest vacant π orbital. In this case the nature and degree of its delocalisation are related to the degree of involvement of phosphorus in the π-electron interaction.

Arylphosphines are reduced over alkali metals at temperatures between −40° and −80°C to the corresponding radical-anions. However, when this method is used, one has to bear in mind the possibility of their conversion into more stable secondary paramagnetic products. Thus, on reducing triphenylphosphine over potassium, Hanna [180] obtained the phosphyls Ph_2PK, which are also formed when triphenylphosphine reacts with lithium and sodium [181], and not the PPh_3^- radical-ions; as a result, his data [180] concerning the structure of PPh_3^- are erroneous. In the ESR spectra of phosphides a_P = 8.0–8.4 G, regardless of the choice of alkali metals; splitting by the protons in the benzene rings is also observed [181]. The true radical-anions derived from triphenylphosphine, methyldiphenylphosphine, and dimethylphenylphosphine were apparently investigated by Kabachnik and coworkers [182,183], who concluded that the spin density is delocalised over several benzene rings. On reduction of dimethylphenylphosphine over potassium at −90°C, Eliseeva et al. [184] obtained an ESR spectrum with splitting by the ^{31}P nucleus and the benzene ring protons. According to these workers [184], the distribution of spin density corresponds to the vacant orbital of benzene stabilised by an electron-accepting substituent. Gerson et al. [185] showed that the Me_2PPh^- radical-ion is stable over sodium at −40°C and confirmed the electron-accepting properties of the dimethylphosphino-group, although their hyperfine splitting constants differ from those quoted by Eliseeva et al. [184], in particular $a_{H(para)}$ = 8.9 G and a_P = 7.2 G. Since the inductive effect of the dimethylphosphino-group should be positive (electron donating), its electron-accepting properties can be accounted for only by an additional interaction of the π electrons of the benzene ring with 3*d* orbitals of phosphorus. The Me_2PPh^- radical-ion is unstable over potassium [185] and is converted into a secondary radical whose ESR spectrum has been published [184] with an erroneous assignment of the splitting constants; the nature of the secondary radical is not clear. Hnoosh and Zingaro [186] established that the radical-anion derived from tris-(α-naphthyl)phosphine is readily converted in the range between 0° and −65°C into naphthalene radical-anions over sodium and into the phosphyls $(C_{10}H_7)_2PK$ over potassium.

A more reliable method of generating phosphine radical-anions is electrochemical reduction, which can be carried out strictly at the reversible electron transfer stage. The formation of the Me_2PPh^- radical-anion was confirmed by this method in combination with ESR spectra [185]. Triphenylphosphine is also reduced at the cathode to a radical-anion [187–189]; the electrochemical reduction of Ph_2PCl and $PhPCl_2$ immediately leads to the elimination of the Cl^- ion, by-passing the radical-anion stage [187]. According to Santhanam and Bard [188] the Ph_3P^- radical-anion is unstable, readily splits off Ph^-, and is then converted into diphenylphosphine. However, when the reduction potential is controlled within the limits corresponding to the one-electron stage, the Ph_3P^- radical-anions can be generated in amounts sufficient for their detection by ESR [189]. Il'yasov et al. [190] refined the proton splitting constants for the Ph_3P^- radical-anion by deuteriating the phenyl groups and confirmed that the unpaired electron is delocalised over all three benzene rings (for further details, see Section VII, 3).

The electrochemical reduction of the phosphines $p\text{-}XC_6H_4P(C{\equiv}CC_6H_4NO_2\text{-}p)_2$ (X = H, Cl, or NMe_2) in tetrahydrofuran or dimethoxyethane [191] results in the formation of radical-ions where the unpaired electron is localised in the fragment $>PC{\equiv}CC_6H_4NO_2\text{-}p$ (a_N = 7.4–7.8 G; a_P = 0.9–1.3 G). The polarogram of the phosphine resembles that of nitrobenzene in a non-aqueous medium. The presence of powerful electron-accepting groups probably prevents the delocalisation of the unpaired electron. The competitive effect of the electron-accepting group is manifested also in the ESR spectra of ethyl benzoates containing the R_2P group in the *para*- or *meta*-positions [192]. For *para*-substituted radical-anions, a_P = 3.8–5.2 G, which is appreciably lower than a_P for the radical-anion derived from dimethylphenylphosphine [185]; for *meta*-substituted radical-anions, a_P = 1.1–1.3 G and the distribution of spin density in the benzene ring changes little compared with the unsubstituted ethyl benzoate.

3. RADICAL-ANIONS DERIVED FROM PHOSPHORINS AND PHOSPHOLES

The ESR spectrum of the radical-anion derived from TPB shows splitting only due to the ^{31}P nucleus (a_P = 32.4 G) or, in other words, the lowest vacant orbital of TPB is more localised at the phosphorus atom than the highest occupied orbital [150,151,193]. A similar phenomenon has been observed also in the ESR spectra of the radical-anions derived from 1,1-dimethoxy- and 1,1-diphenoxy-TPB (a_P = 31.6 G) [152]. For the ESR spectrum of the TPB radical-trianion, a_P = 4.6 G. [151] Märkl and Merz [154] reported radical-anions derived from 1,1-diaryl-TPB.

Thomson and Kilcast [194] obtained the radical-anions derived from 1-R-2,5-diphenylphospholes: a_P = 23.5 G for R = Me and a_P = 26.5 G for R = Ph. On the basis of these results, and Dimroth's ESR data [152–154] for the phosphorin radical-anions and radical-cations, Thomson and Kilcast [194] attempted to estimate the constant Q^P_{eff} for the σ–π polarisation at the phosphorus atom. The spin density

$\rho\pi$(P) was calculated by the McLachlan method. Q^P_{eff} = 97.9 G was found from the aP for the phosphorin radical-cations, which is close to the values of Q^P_{eff} obtained from aP for $\dot{P}H_2$, $\dot{P}F_2$, AND $\dot{P}Cl_2$ and from calculations on these radicals by the CNDO/2 method[23]. The values of Q^P_{eff} obtained from the aP for the radical-anions derived from phosphorins and phospholes are 31.7 and 725.4 G respectively. The ^{31}P σ–π interaction constants probably depend strongly on the charge at the phosphorus and adjoining atoms. Thomson and Kilcast[194] attempted to take into account the influence of the adjoining atom in the two-parameter equation $a_P = Q^P_{PP}\rho(P) + Q^P_{CP}\rho(C)$ and found that Q^P_{PP} = 39 G and Q^P_{CP} = 28.6 G.

4. PENTAATOMIC RADICAL-ANIONS

All the radical-anions of this type which have been studied experimentally were obtained by the low-temperature γ-irradiation of solids. The ESR spectra of the $\dot{P}O_4^{2-}$ radical-ion in irradiated phosphates and pyrophosphates have been studied in a number of investigations[127, 195-197]; aP depends on the environment of the radical, as for $\dot{P}O_3^{2-}$. The hypothesis[127] that $\dot{P}O_3$ and not $\dot{P}O_4^{2-}$ is formed in many cases has been confirmed to some extent by a quantum-chemical calculation[23], although its results require serious revision.

The ESR spectrum of a radical which Symons identified[199] as $\dot{P}O_4^{4-}$ was observed for irradiated phenacite[198]; this identification is probably correct[200]. The value of aP for $\dot{P}O_4^{4-}$ is much higher than for $\dot{P}(OR)_4$ radicals[92-94] (Tables 5 and 9). This result is strange from the standpoint of the general rule concerning the increase of aP for $\dot{P}X_4$ with increasing electronegativity of the ligand X,[13, 40] particularly since aP = 860 G for the $(MeO)_3PO^{\cdot-}$ radical-anion, formed[40] in γ-irradiated phosphate together with $Me_2\dot{P}O$, which is less than the value for $\dot{P}(OMe)_4$. The "$\dot{P}O_4^{4-}$ anomaly" has been explained[40] by the influence of the surrounding Be^{2+} cations; it is suggested that aP < 900 G for $\dot{P}O_4^{4-}$ in weaker fields. In the $PO_3F^{\cdot-}$ radical-anion the unpaired electron is highly localised at the oxygen atom[88].

A quantum-chemical calculation[102] for the hypothetical $PH_3O^{\cdot-}$ radical-anion by the CNDO/2 method showed that its equilibrium geometry is almost the same as that of PH_3OH (Table 6), namely trigonal bypyramidal. This result is consistent with the data of Begum and Symons[41] and also of Gillbro and Williams[201] for the ESR spectrum of $POCl_3^{\cdot-}$ radical-anions; in both cases there is splitting by the two equivalent ^{35}Cl nuclei corresponding to the axial positions and a smaller splitting due to the third (equatorial) ^{35}Cl nucleus. The radical-anions have been generated[41] in polycrystalline $POCl_3$, which led to unduly high constants for isotropic splitting by axial ^{35}Cl. A study[201] of the ESR spectra of the radical-anions in irradiated $POCl_3$ single crystals showed that these constants are consistent with data[98] obtained from the ESR spectra of chlorophosphoranyl radicals in solutions. Consequently the chlorine atom in these radicals is fixed in the axial position and there is no pseudorotation. Furthermore, anisotropic splitting by the axial ^{35}Cl ($B_{||}$ = 30 G), corresponding to a spin density of 0.29 in the $3p\sigma$ chlorine orbital, has been observed[201].

According to calculations[102], the distribution of spin density in the $PH_3O^{\cdot-}$ radical-anion differs significantly from that in the neutral $\dot{P}H_3OH$ radical; in particular the s spin density at the phosphorus atom is reduced by an order of magnitude in the radical-anion.

5. THE RADICAL-ANIONS DERIVED FROM PHOSPHINE OXIDES AND PHOSPHATES

Begum and Symons[43] reported that the $Me_3PO^{\cdot-}$ radical-anion, whose aP is fully consistent with the ESR data for $Me_3POBu\text{-}t$[91] (splitting by methyl protons was not observed[43]), is formed in γ-irradiated trimethylphosphine oxide. This result is inconsistent with the above data obtained by quantum-chemical calculation[102]. It is therefore more likely that Begum and Symons[43] obtained the ESR spectrum of the $Me\dot{P}OH$ [$Me_2\dot{P}OH$? (Ed. of Translation)] radical.

The radical-anions derived from triphenylphosphine oxide[182,183,202], trialkyl phosphine oxides[182,183,203], and alkylarylphosphine oxides[182,183] are formed when these compounds are reduced over an alkali metal in tetrahydrofuran or dimethoxyethane. Il'yasov and coworkers[189,204] showed that, in the electrochemical reduction of triphenylphosphine oxide, triphenylphosphine sulphide, and diethyl β-styrylphosphinate, the first stage is reversible addition of one electron.

The ESR spectra of the radical-anions of all the above compounds generated by this method have been investigated[189,205]. For an unambiguous assignment of the splitting constants in the ESR spectra, a study was also made[190] of the radical-anions $Ph_2(C_6D_5)PO^{\cdot-}$, $Ph(C_6D_5)_2PO^{\cdot-}$, and $(C_6D_5)_3PO^{\cdot-}$. It was established that, as in the triphenylphosphine radical-anion, the unpaired electron is equally delocalised over all three benzene rings and also over the phosphorus atom (aP = 4 G). Such delocalisation cannot be accounted for within the framework of the π-electron model; the unsatisfactory result of the calculation on $Ph_3PO^{\cdot-}$ by the Hückel method confirmed this. Possibly it is dynamic, as in the radical-anions derived from tetraphenylsilane and diethyldiphenylsilane[206], the main feature of such delocalisation being a marked dependence of the rate of electron transfer from one aromatic fragment to another on the counterion solvation conditions[207]. Cowley and Hnoosh[208] studied the $Ph_2(NMe_2)PO^{\cdot-}$ radical-anions generated by reduction over metallic sodium. It follows from the ESR spectra obtained[208] that the spin density is delocalised over the phosphorus atom and one benzene ring; the splitting constants for the $Ph(NH_2)MePO^{\cdot-}$ radical-anion are aP = 8.75 G, aH(para) = aH(ortho) = 3.5 G, $a_{H(Me)}$ = 0.38 G, and a_N = 4.9 G. The π conjugation of the phosphoryl group with the benzene ring probably occurs more readily than with other substituents. Calculation of the spin densities in terms of the π approximation by the McLachlan method gives rise to a satisfactory agreement with experiment. Kabachnik and coworkers[192] generated the m- and p-$R_2P(O)C_6H_4COOEt$ (R = Me, Et, or i-PrNMe$_2$) radical-anions by electrochemical reduction in acetonitrile at –40°C. The ^{31}P splitting in the ESR spectra of the *para*-substituted radical-anions is fairly large (aP ≃ 13 G), increasing somewhat with increase of the bulk of R; slight splitting due to the R protons has also been observed (a = 0.3–0.6 G). The ESR spectra of *meta*-substituted radical-anions are characterised by the absence of splitting due to ^{31}P and the protons in R; other splitting constants differ little from those for the ethyl benzoate radical-anion. The splitting constants for the protons in the *ortho*-position relative to the ethoxycarbonyl group are correlated with the constants $\sigma_{eff} = \sigma_{R(m)} + 0.23\sigma_I$ of the substituents R_2P, $R_2P(O)$, $R_2P(S)$, and simpler groups.

Allen and Bond[209] studied the radical-anions obtained from semiquinone-phosphates derived from benzo- and

naphtho-quinones. a_P = 1.3 G for the p-$OC_6H_4O\dot{P}O_3^{2-}$ radical-anion; after the introduction of four methyl groups, a_P = 17.2 G. Allen and Bond[209] believe that the hyperconjugation model, in which the spin density is transferred directly from the $2p\pi$ orbital of carbon to the 3s orbital of phosphorus, is most suitable for these radical-anions; spin polarisation is less likely. Gulick and Geske[210] generated radical-anions derived from dialkyl p-nitrophenyl and diaryl p-nitrophenyl phosphates by electrochemical reduction and observed in their ESR spectra splitting due to the protons of the p-nitrophenyl group and the ^{14}N and ^{31}P nuclei. The splitting constant a_P = 7–8 G, increasing to 13.6 G for the $(EtO)_2P(O)CH_2C_6H_4NO_2$-$p^{\cdot-}$ radical-anion. They suggested[210] that the transfer of spin density to phosphorus takes place via a hyperconjugation mechanism, although a_P did not change in the range from +25° to −45°C. Gulick[211] interpreted the splittings by the ^{31}P nucleus in the ESR spectra of the radical-anions derived from O-(diphenylphosphoryl)-2,6-di-R-4-nitrophenols in terms of a compound model combining the spin polarisation and hyperconjugation effects. For the $(PhO)_2$.$P(O)SC_6H_4NO_2$-$p^{\cdot-}$ radical-anion, a_P = 24.8 G, either in consequence of direct π conjugation due to the 3d sulphur orbitals or because the PSC valence angle is smaller than the POC angle, which leads to a greater degree of transfer of spin density to phosphorus via the hyperconjugation mechanism. The values of a_N and the potentials $E_{\frac{1}{2}}$ for the radical-anions which he investigated[211], led Gulick to the conclusion that the electronic effects of the $Ph_2P(O)O$ group and the hydrogen atom are approximately the same.

Lassmann et al.[212] established that the splitting constants a_N and a_P for the ESR spectra of the radical-anions derived from diethyl p-nitrophenyl phosphate (paraoxon) and dimethyl p-nitrophenyl phosphate (parathion) are somewhat different. Furthermore, they depend on the anion of the salt used as the supporting electrolyte: a_P is 6.12 G for the parathion radical-anion with NEt_4I and 9.71 G with NEt_4ClO_4. Evidently the radical-anions generated electrochemically form association complexes with the ions of the supporting electrolytes; the spin densities at the phosphoryl group and other polar groups are sensitive to the nature of these complexes.

The $PhP(O)Cl_2^{\cdot-}$ radical-anion, generated by the γ-irradiation of $PhP(O)Cl_2$ at −196°C [216], has a trigonal bipyramidal structure with appreciable localisation of the unpaired electron at the s orbital of phosphorus, as in $POCl_3^{\cdot-}$ (Table 9). When there are two possible ways of adding an electron to the molecule (to the phosphorus atom or the benzene ring), the preferred mode of addition probably depends on the relative electron affinities of the two centres and at low temperatures also on the degree of distortion necessary for the formation of the most stable conformation of the radical-anion[217]. The three-centre σ^* Cl–P–Cl molecular orbital should therefore lie below the π^* molecular orbital of the benzene ring.

6. RADICAL-ANIONS WITH A P = N BOND

The ESR spectra of the $R_3PNC_6H_4NO_2$-$p^{\cdot-}$ radical-anions derived from phosphazo-compounds and generated at the cathode in acetonitrile or dimethylformamide have been investigated[218–220]; the first stage of the electrochemical reduction of these substances is a reversible one-electron process[221]. The splitting constants are $a_{N(NO_2)}$ = 11.0–13.5 G and a_P = 3.5–5.5 G; both constants depend on the electron density of the substituents R. If one of these is R = Ph, a slight (0.2–0.3 G) splitting by the protons of this benzene ring is also observed. The authors[218–220] concluded that the radical-anions from phosphazoarenes contain a π-electron system incorporating the phosphazo-group. The π-electronic structure of the phosphazoarenes and the spin densities were calculated on this hypothesis by the Hückel and McLachlan methods respectively[222]. The calculated energies of the lowest vacant π orbitals are correlated with the potentials $E_{\frac{1}{2}}$ of the phosphazoarenes[221] and the splitting constants found from the calculated spin densities agree very well with experiment. The splitting by the ^{14}N nucleus of the imino-nitrogen does not exceed 0.2 G according to the calculation[222] and is not therefore observed in the ESR spectra[218,219].

The unpaired electron in the $Ph_3PNXC_6H_4NO_2$-$p^{\cdot-}$ (X = S or SO) radical-anions is delocalised only over the p-nitrophenyl residue[218]. Thus the –S– and –SO– bridging groups prevent the inclusion of the phosphazo-group in the π-conjugation system. This system also breaks down in the $(p\text{-}F_3CC_6H_4)_3POC_6H_4NO_2$-$p$ radical-anion, the ESR spectrum of which resembles that of the p-nitroaniline radical-anion[219]; in this case the 3d orbitals of phosphorus are probably involved preferentially in the formation of the P–R bond and not P–N.

Allcock and Birdsall[223] generated the $(PNR_2)_3^{\cdot-}$ radical-anions where R = Ph or OAr, by an electrochemical method in dimethylformamide; under these conditions, $(PNF_2)_3$ and $(PNCl_2)_3$ are not reduced to the radical-anions. It follows from the ESR spectra of the radical-anions obtained by Allcock and Birdsall[223] that the unpaired electron is not delocalised over the phosphazene ring. This conclusion was fully confirmed by Mishra and Symons[224], who obtained the ESR spectrum of $(PNCl_2)_3^{\cdot-}$ on low-temperature γ-irradiation of the phosphonitrilic chloride trimer. It is characterised by an appreciable isotropic splitting by one of the ^{31}P nuclei. Thus the unpaired electron is localised at one phosphorus atom, whose hybridisation probably corresponds to the configuration of a trigonal bipyramid, as in phosphoranyl radicals.

7. THE $PF_5^{\cdot-}$ RADICAL-ANION

Morton[67] observed the isotropic ESR spectrum of a radical containing a phosphorus atom and four equivalent fluorine atoms on irradiation of NH_4PF_6 at about 20°C [67]; the radical was identified as $\dot{P}F_4$. Atkins and Symons[68] observed a similar spectrum on γ-irradiation of KPF_6 and noted that it becomes appreciably broadened at −63°C; at −73°C and below the fluorine atoms become non-equivalent, which is believed to be a consequence of the "freezing" of the pseudorotation in PF_4. Mishra and Symons showed recently[225] that an additional doublet splitting is observed in this spectrum (a = 2.3 G); consequently the paramagnetic species formed is the radical-anion $PF_5^{\cdot-}$ and not $\dot{P}F_4$. This process is more likely also on general grounds. Four fluorine atoms in $PF_5^{\cdot-}$ remain equivalent also at both 20° and −196°C; the broadening of the components of the ESR spectrum observed by Atkins and Symons[68] can be explained by the hindered rotation of the entire radical-anion and not by pseudorotation.

---o0o---

On the whole one may conclude that the free radicals and radical-ions derived from phosphorus compounds constitute a fairly specific class of radical species. Only the properties of phosphinyl radicals resemble those of

aminyl radicals to which the former are formally analogous. The properties of other phosphorus-containing free radicals are determined to a large extent by the characteristics of the nature of the chemical bonds involving phosphorus relative to those of the elements in the Second Period. A detailed study of their properties is undoubtedly important for the development of ideas concerning the stereochemistry and reactivity of phosphorus compounds.

REFERENCES

1. J.R. Van Wazer, "Phosphorus and Its Compounds", (Translated into Russian), Inostr. Lit., Moscow, 1962, p. 90.
2. R.H. Dalton and C.N. Hinshelwood, Proc. Roy. Soc. (A), 125, 294 (1929).
3. M.S. Kharasch, E.V. Jensen, and W.H. Urry, J. Amer. Chem. Soc., 67, 1864 (1945).
4. L.Z. Soborovskii, Yu.M. Zinov'ev, and M.A. Englin, Dokl. Akad. Nauk SSSR, 67, 293 (1949); 73, 333 (1950).
5. C. Walling and M.S. Pearson, "Topics in Phosphorus Chemistry", Interscience Publishers, New York–London–Sydney, 1966, Vol. 3, p. 1.
6. R.F. Hudson, "Organic Chemistry", Vol. 6, "Structure and Mechanism in Organophosphorus Chemistry", (Translated into Russian), Izd. Mir, Moscow, 1967.
7. H. Horsfield, J.R. Morton, and D.H. Whiffen, Mol. Phys., 4, 475 (1961).
8. J.K. Wan, J.R. Morton, and H.J. Bernstein, Canad. J. Chem., 44, 1957 (1966).
9. R.W. Fessenden and R.H. Schuler, J. Chem. Phys., 45, 1845 (1966).
10. W. Nelson, G. Jackel, and W. Gordy, J. Chem. Phys., 52, 4572 (1970).
11. R.W. Rudolph, R.C. Taylor, and R.W. Parry, J. Amer. Chem. Soc., 88, 3729 (1966).
12. M.S. Wei, J.H. Current, and J. Gendell, J. Chem. Phys., 52, 1592 (1970).
13. G.F. Kokoszka and F.E. Brinckmann, J. Amer. Chem. Soc., 92, 1199 (1970).
14. L. Andrews and D.L. Frederick, J. Phys. Chem., 73 2774 (1969).
15. T. Kennedy and R.S. Sinclair, J. Inorg. Nuclear Chem., 32, 1125 (1970).
16. D.A. Ramsay, Nature, 178, 374 (1956).
17. R.N. Dixon, G. Dixbury, and D.A. Ramsay, Proc. Roy. Soc. (A), 296, 137 (1967).
18. D. Solan and P.L. Timms, Chem. Comm., 1968, 1541.
19. R.L. Morehouse, J.J. Christiansen, and W. Gordy, J. Chem. Phys., 45, 1747 (1966).
20. S. Sugimoto, K. Kuwata, S. Ohnishi, and I. Nitta, Nippon Hoshasen Kobunshi Kenkyu Kyokai Nempo, 7, 199 (1965).
21. S.K. Wong and J.K. Wan, Spectroscopy Letters, 3, 135 (1970).
22. K.U. Ingold, J. Chem. Soc., Perkin II, 1973, 420.
23. D. Kilcast and C. Thomson, J. Chem. Soc., Faraday II, 1972, 435.
24. J.C. Cobb, and A. Hinchliffe, Chem. Phys. Letters, 24, 75 (1974).
25. J. Pellon, J. Polymer Sci., 43, 537 (1960).
26. M.L. Kaufman and C.E. Griffin, Tetrahedron Letters, 769 (1965).
27. L. Horner and J. Dörges, Tetrahedron Letters, 763 (1965).
28. R.S. Davidson, R.A. Sheldon, and S. Trippett, J. Chem. Soc. (C), 722 (1966).
29. S.K. Wong, W. Sytnyk, and J.K. Wan, Canad. J. Chem., 49, 994 (1971).
30. J. Pellon, J. Amer. Chem. Soc., 83, 1915 (1961).
31. M.M. Rauhut, H.A. Currier, A.M. Semsel, and V.P. Wystrach, J. Org. Chem., 26, 5138 (1961).
32. B.A. Arbuzov, G.M. Vinokurova, and I.A. Aleksandrova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1962, 290.
33. G.M. Burch, H. Goldwhite, and R.N. Haszeldine, J. Chem. Soc., 1963, 1083.
34. R. Brandon, R.N. Haszeldine, and P.J. Robinson, J. Chem. Soc., Perkin II, 1973, 1295.
35. J.R. Little and P.F. Hartman, J. Amer. Chem. Soc., 88, 96 (1966).
36. T. Saegusa, Y. Ito, N. Yasuda, and T. Hotaka, J. Org. Chem., 35, 4238 (1970).
37. C.M.L. Kerr, K. Webster, and F. Williams, Mol. Phys., 25, 1461 (1973).
38. K. Terauchi and H. Sakurai, Bull. Chem. Soc. Japan, 41, 1736 (1968).
39. A.G. Davies, D. Griller, and B.P. Roberts, J. Amer. Chem. Soc., 94, 1782 (1972).
40. I.S. Ginns, S.P. Mishra, and M.C.R. Symons, J. Chem. Soc., Dalton, 1973, 2509.
41. A. Begum and M.C.R. Symons, J. Chem. Soc. (A), 1971, 2065.
42. M. Geoffroy and E.A.C. Lucken, Mol. Phys., 22, 257 (1971).
43. A. Begum and M.C.R. Symons, J. Chem. Soc., Faraday II, 1973, 43.
44. Ya.A. Levin, A.V. Il'yasov, D.G. Pobedimskii, E.I. Gol'dfarb, I.I. Saidashev, and Yu.Yu. Samitov, Izv. Akad. Nauk SSSR, Ser. Khim., 1970, 1680.
45. Ya.A. Levin, A.V. Il'yasov, and E.I. Gol'dfarb, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 1676.
46. D.G. Pobedimskii, Yu.Yu. Samitov, E.I. Gol'dfarb, and P.A. Kirpichnikov, Teor. Eksper. Khim., 8, 327 (1972).
47. Ya.A. Levin, A.V. Il'yasov, E.I. Gol'dfarb, and E.I. Vorkunova, Org. Magn. Resonance, 5, 487 (1973).
48. D.G. Pobedimskii, P.A. Kirpichnikov, Yu.Yu. Samitov, and E.I. Gol'dfarb, Org. Magn. Resonance, 5, 503 (1973).
49. A.R. Stiles, W.E. Vaughan, and F.F. Rust, J. Amer. Chem. Soc., 80, 714 (1958).
50. A.N. Pudovik and I.V. Konovalova, Zhur. Obsch. Khim., 29, 3342 (1959).
51. A.N. Pudovik, I.V. Konovalova, and O.S. Durova, Zhur. Obsch. Khim., 31, 2656 (1961).
52. E.F. Bugerenko, E.A. Chernyshev, and A.D. Petrov, Dokl. Akad. Nauk SSSR, 143, 840 (1962).
53. M.I. Kabachnik, Chung-Yu Chang, and E.N. Tsvetkov, Zhur. Obsch. Khim., 32, 3351 (1962).
54. N. Kornblum, G.D. Cooper, and J.E. Taylor, J. Amer. Chem. Soc., 72, 3013 (1950).
55. G.P. Miklukhin and A.F. Rekasheva, Dokl. Akad. Nauk SSSR, 85, 827 (1952).
56. A.F. Levit, L.A. Kiprianova, and I.P. Gragerov, Dokl. Akad. Nauk SSSR, 213, 634 (1973).
57. E.F. Jason, and E.K. Fields, J. Org. Chem., 27, 1402 (1962).
58. B.A. Arbuzov and L.M. Kataeva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1962, 172.
59. B.A. Arbuzov and Ching-Ling Chang, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1963, 1934, 1941, 1945.

60. J. Michalski, W. Stec, and A. Zwierzak, Chem. Ind., 1965, 347.
61. T. Kaufmann, G. Ruckelshaus, and D. Glindemann, Chem. Ber., 106, 1618 (1973).
62. G. Wittig and G. Geissler, Annalen, 580, 44 (1953).
63. G. A. Razuvaev and N. A. Osanova, Dokl. Akad. Nauk SSSR, 104, 552 (1955).
64. G. A. Razuvaev, G. G. Petukhov, and N. A. Osanova, Dokl. Akad. Nauk SSSR, 104, 733 (1955).
65. G. A. Razuvaev, G. G. Petukhov, and N. A. Osanova, Zhur. Obsch. Khim., 31, 2191 (1961).
66. G. A. Razuvaev, N. A. Osanova, and I. A. Shlyapnikova, Zhur. Obsch. Khim., 27, 1466 (1957).
67. J. R. Morton, Canad. J. Phys., 41, 706 (1963).
68. P. W. Atkins and M. C. R. Symons, J. Chem. Soc., 1964, 4363.
69. D. P. Wyman, J. Y. C. Wang, and W. R. Freeman, J. Org. Chem., 28, 3173 (1963).
70. D. Hellwinkel, Chem. Ber., 102, 528 (1969).
71. D. Griller and B. P. Roberts, J. Organomet. Chem., 42, C47 (1972).
72. D. Griller and B. P. Roberts, J. Chem. Soc., Perkin II, 1973, 1416.
73. L. Horner and A. Mentrup, Annalen, 646, 65 (1961).
74. L. Horner and J. Haufe, J. Electroanalyt. Chem., 20, 245 (1969).
75. O. A. Rebrova, N. A. Nesmeyanov, V. V. Mikul'shina, and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 398.
76. G. Kamai and F. M. Kharrasova, Zhur. Obsch. Khim., 27, 953 (1957),
77. F. Ramirez and N. McKalvie, J. Amer. Chem. Soc., 79, 5829 (1957).
78. C. Walling and R. Rabinowitz, J. Amer. Chem. Soc., 79, 5326 (1957).
79. C. Walling and R. Rabinowitz, J. Amer. Chem. Soc., 81, 1243 (1959).
80. C. Walling, O. H. Basedow, and E. S. Savas, J. Amer. Chem. Soc., 82, 2181 (1960).
81. D. G. Pobedimskii, N. A. Mukmeneva, and P. A. Kirpichnikov, Uspekhi. Khim., 41, 1242 (1972) [Russ. Chem. Rev., No. 7 (1972)].
82. S. A. Buckler, J. Amer. Chem. Soc., 84, 3093 (1962).
83. W. G. Bentrude and R. A. Wielesek, J. Amer. Chem. Soc., 91, 2406 (1969).
84. W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Chem. Comm., 1969, 296.
85. Ya. A. Levin, A. V. Il'yasov, E. I. Gol'dfarb, and E. I. Vorkunova, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 1673.
86. Ya. A. Levin, A. V. Il'yasov, E. I. Gol'dfarb, and E. I. Vorkunova, Org. Magn. Resonance, 5, 497 (1973).
87. C. A. McDowell, K. A. R. Mitchell, and P. Raghunathan, J. Chem. Phys., 57, 1699 (1972).
88. A. Begum, S. Subramanian, and M. C. R. Symons, J. Amer. Chem. Soc. (A), 1970, 1323.
89. J. K. Kochi and P. J. Krusic, J. Amer. Chem. Soc., 91, 3944 (1969).
90. J. K. Kochi and P. J. Krusic, Chem. Soc. Spec. Publication, 1970, No. 24, 47.
91. P. J. Krusic, W. Mahler, and J. K. Kochi, J. Amer. Chem. Soc., 94, 6033 (1972).
92. A. G. Davies, D. Griller, and B. P. Roberts, Angew. Chem., 83, 800 (1971).
93. A. G. Davies, D. Griller, and B. P. Roberts, J. Chem. Soc., Perkin II, 1972, 993.
94. A. G. Davies, D. Griller, and B. P. Roberts, J. Chem. Soc., Perkin II, 1972, 2224.
95. A. G. Davies, R. W. Dennis, D. Griller, and B. P. Roberts, J. Organomet. Chem., 40, C33 (1972).
96. R. W. Dennis and B. P. Roberts, J. Organomet. Chem., 43, C2 (1972).
97. R. W. Dennis and B. P. Roberts, J. Organomet. Chem., 47, C8 (1973).
98. D. Griller and B. P. Roberts, J. Chem. Soc., Perkin II, 1973, 1339.
99. S. B. Pierce and C. D. Cornwell, J. Chem. Phys., 48, 2118 (1968).
100. A. G. Davies, R. W. Dennis, D. Griller, K. U. Ingold, and B. P. Roberts, Mol. Phys., 25, 989 (1973).
101. J. Higuchi, J. Chem. Phys., 50, 1001 (1969).
102. V. V. Penkovsky and Yu. I. Gorlov, "V International Conference of Organic Phosphorus Chemistry, Gdansk, 1974, Abstracts", p. 78.
103. E. L. Muetterties, W. Mahler, and R. Schmutzler, Inorg. Chem., 2, 613 (1963); 3, 1298 (1964).
104. P. J. Krusic and P. Meakin, Chem. Phys. Letters, 18, 347 (1973).
105. G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, Chem. Comm., 1974, 118.
106. A. G. Davies, M. J. Parrot, and B. P. Roberts, Chem. Comm., 1974, 973.
107. A. G. Davies, M. J. Parrot, and B. P. Roberts, Chem. Comm., 1974, 27.
108. W. G. Bentrude and T. B. Min, J. Amer. Chem. Soc., 94, 1025 (1972).
109. R. E. Atkinson, J. I. G. Cadogan, and J. T. Sharp, J. Chem. Soc. (B), 1969, 138.
110. R. S. Davidson, Tetrahedron, 25, 3383 (1969).
111. J. -J. L. Fu and W. G. Bentrude, J. Amer. Chem. Soc., 94, 7710 (1972).
112. J. -J. L. Fu, W. G. Bentrude, and C. E. Griffin, J. Amer. Chem. Soc., 94, 7717 (1972).
113. W. G. Bentrude, E. R. Hansen, W. A. Khan, and P. E. Rogers, J. Amer. Chem. Soc., 94, 2867 (1972).
114. W. G. Bentrude, E. R. Hansen, W. A. Khan, T. B. Min, and P. E. Rogers, J. Amer. Chem. Soc., 95, 2286 (1973).
115. W. G. Bentrude, J. -J. L. Fu, and P. E. Rogers, J. Amer. Chem. Soc., 95, 3625 (1973).
116. T. R. Emerson and C. W. Rees, J. Chem. Soc. 1962, 1917.
117. E. Furimsky and J. A. Howard, J. Amer. Chem. Soc., 95, 369 (1973).
118. G. B. Watts and K. U. Ingold, J. Amer. Chem. Soc., 94, 2528 (1972).
119. F. R. Mayo, L. J. Durham, and K. S. Griggs, J. Amer. Chem. Soc., 85, 3156 (1963).
120. B. Fontal and H. Goldwhite, J. Org. Chem., 31, 3804 (1966).
121. Ya. A. Levin, E. K. Trutneva, and B. E. Ivanov, Zhur. Obsch. Khim., 44, 1443 (1974).
122. E. A. C. Lucken, J. Chem. Soc. (A), 1966, 1354.
123. A. R. Metcalfe and W. A. Waters, J. Chem. Soc. (B), 1967, 340.
124. A. Begum, S. Subramanian, and M. C. R. Symons, J. Chem. Soc. (A), 1970, 1334.
125. C. M. L. Kerr, K. Webster, and F. Williams, J. Phys. Chem., 76, 2848 (1972).
126. P. J. Krusic and J. K. Kochi, J. Amer. Chem. Soc., 91, 6161 (1969).

127. P.W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals. An Application of Electron Spin Resonance to the Study of Molecular Structure". (Translated into Russian), Izd. Mir, Moscow, 1970.
128. W. Damerau, G. Lassmann, and K. -H. Lohs, Z. Chem., 11, 182 (1971).
129. W. Damerau, G. Lassmann, and K. -H. Lohs, J. Magn. Resonance, 5, 408 (1971).
130. T. Kawamura and J. K. Kochi, J. Amer. Chem. Soc., 94, 648 (1972).
131. M. C. R. Symons, J. Amer. Chem. Soc., 94, 8589 (1972).
132. A. Begum, A. R. Lyons, and M. C. R. Symons, J. Chem. Soc. (A), 1971, 2388.
133. A. E. Arbuzov, F. G. Valitova, A. V. Il'yasov, B. M. Kozyrev, and Yu. V. Yablokov, Dokl. Akad. Nauk SSSR, 147, 839 (1962).
134. F. G. Valitova and Yu. M. Ryzhmanov, Dokl. Akad. Nauk SSSR, 170, 1124 (1966).
135. A. Begum, A. R. Lyons, and M. C. R. Symons, J. Chem. Soc. (A), 1971, 2290.
136. A. R. Lyons and M. C. R. Symons, J. Amer. Chem. Soc., 95, 3484 (1973).
137. A. R. Lyons and M. C. R. Symons, J. Chem. Soc., Faraday II, 1972, 622.
138. A. R. Lyons, G. W. Neilson, and M. C. R. Symons, Chem. Comm., 1972, 507.
139. F. Ramirez and S. Dershowitz, J. Amer. Chem. Soc., 78, 5614 (1956).
140. F. Ramirez and S. Dershowitz, J. Amer. Chem. Soc., 81, 587 (1959).
141. E. A. C. Lucken, F. Ramirez, V. P. Catto, D. Rhum, and S. Dershowitz, Tetrahedron, 22, 637 (1966).
142. P. D. Bartlett, E. F. Cox, and R. E. Davis, J. Amer. Chem. Soc., 83, 103 (1961).
143. E. A. C. Lucken, J. Chem. Soc., 1963, 5123.
144. E. Müller, H. Eggensperger, B. Teissler, and K. Scheffler, Z. Naturforsch., 18b, 984 (1963).
145. E. Müller, H. Eggensperger, and K. Scheffler, Annalen, 658, 103 (1962).
146. G. Boekestein, W. G. Voncken, E. H. J. M. Jansen, and H. M. Buck, Rec. Trav. chim., 93, 69 (1974).
147. M. Finkelstein, J. Org. Chem., 27, 4076 (1962).
148. R. L. Powell and C. D. Hall, J. Amer. Chem. Soc., 91, 5403 (1969).
149. K. Dimroth, N. Greif, H. Perst, and F. Steuber, Angew. Chem., 79, 58 (1967).
150. K. Dimroth, N. Greif, W. Städe, and F. Steuber, Angew. Chem., 79, 725 (1967).
151. K. Dimroth, Colloq. CNRS, 1970, No. 182.
152. K. Dimroth and W. Städe, Angew. Chem., 80, 966 (1968).
153. K. Dimroth, A. Hettche, W. Städe, and F. Steuber, Angew. Chem., 81, 784 (1969).
154. G. Märkl and A. Merz, Tetrahedron Letters, 1969, 1231.
155. E. A. C. Lucken and C. Mazeline, J. Chem. Soc. (A), 1966, 1074; 1967, 439.
156. A. R. Lyons, G. W. Neilson, and M. C. R. Symons, J. Chem. Soc., Faraday II, 1972, 807.
157. E. A. C. Lucken, J. Chem. Soc. (A), 1966, 1357.
158. H. M. Buck, A. H. Huizer, S. J. Oldenburg, and P. Schipper, Rec. Trav. chim., 89, 1085 (1970).
159. H. M. Buck, A. H. Huizer, S. J. Oldenburg, and P. Schipper, Phosphorus, 1, 97 (1971).
160. R. J. Boyd and M. A. Whitehead, J. Chem. Soc., Dalton, 1972, 81.
161. L. J. Aarons, M. F. Guest, M. B. Hall, and I. H. Hillier, J. Chem. Soc., Faraday II, 1973, 643.
162. Yu. I. Gorlov, I. I. Ukrainsky, and V. V. Penkovsky, Theoret. Chim. Acta (Berl.), 34, 31 (1974).
163. D. R. Dalton and S. A. Liebman, J. Amer. Chem. Soc., 91, 1194 (1969).
164. R. D. Rieke, R. A. Copenhafer, A. M. Aguiar, M. S. Chattha, and J. C. Williams, Chem. Comm., 1972, 1130.
165. M. Hanna and L. J. Altman, J. Chem. Phys., 36, 1788, (1962).
166. J. R. Morton, J. Phys. Chem. Solids, 24, 209 (1963).
167. J. R. Morton, Mol. Phys., 6, 193 (1963).
168. F. G. Herring, J. H. Hwang, W. C. Lin, and C. A. McDowell, J. Phys. Chem., 70, 2487 (1966).
169. A. Serway and S. A. Marshall, J. Chem. Phys., 45, 4098 (1966).
170. S. Schlick, B. L. Silver, and Z. Luz, J. Chem. Phys., 52, 1232 (1970).
171. J. R. Morton, Mol. Phys., 5, 217 (1962).
172. P. W. Atkins, N. Keen, and M. C. R. Symons, J. Chem. Soc., 1963, 250.
173. R. W. Fessenden, J. Magn. Resonance, 1, 227 (1969).
174. A. Begum, S. Subramanian, and M. C. R. Symons, J. Chem. Soc. (A), 1971, 700.
175. A. L. J. Beckwith, Austral. J. Chem., 25, 1887 (1972).
176. B. C. Gilbert, J. P. Larkin, R. O. C. Norman, and P. M. Storey, J. Chem. Soc., Perkin II, 1972, 1508.
177. M. Geoffroy and E. A. C. Lucken, Mol. Phys., 24, 335 (1972).
178. M. C. R. Symons, J. Chem. Soc. (A), 1970, 1998.
179. G. Adevik and G. Lagercrantz, Acta Chem. Scand., 24, 2253 (1970).
180. M. Hanna, J. Chem. Phys., 37, 685 (1962).
181. A. D. Britt and E. T. Kaiser, J. Phys. Chem., 69, 2775 (1965).
182. M. I. Kabachnik, Tetrahedron, 20, 655 (1964).
183. M. I. Kabachnik, V. V. Voevodskii, T. A. Mastryukova, S. P. Solodovnikov, and T. A. Melent'eva, Zhur. Obsch. Khim., 34, 3234 (1964).
184. N. V. Eliseeva, D. A. Sharpatyi, and A. N. Pravednikov, Zhur. Strukt. Khim., 7, 511 (1966).
185. F. Gerson, H. Plattner, and H. Bock, Helv. Chim. Acta, 53, 1629 (1970).
186. M. H. Hnoosh and R. A. Zingaro, J. Amer. Chem. Soc., 92, 4388 (1970).
187. R. E. Dessy, T. Chivers, and W. Kitching, J. Amer. Chem. Soc., 88, 467 (1966).
188. K. S. V. Santhanam and A. J. Bard, J. Amer. Chem. Soc., 90, 1118 (1968).
189. A. V. Il'yasov, Yu. M. Kargin, Ya. A. Levin, I. D. Morozova, B. V. Mel'nikov, A. A. Vafina, N. N. Sotnikova, and V. S. Galeev, Izv. Akad. Nauk SSSR, Ser. Khim., 1971, 770.
190. A. V. Il'yasov, Ya. A. Levin, I. D. Morozova, A. A. Vafina, I. P. Gozman, and E. I. Zoroatskaya, Dokl. Akad. Nauk SSSR, 201, 108 (1971).
191. S. P. Solodovnikov, A. I. Bokanov, L. I. Chekunina, and B. I. Stepanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1973, 205.
192. A. I. Prokof'ev, S. P. Solodovnikov, I. G. Malakhova, E. N. Tsvetkov, and M. I. Kabachnik, Zhur. Obsch. Khim., 43, 2621 (1973).
193. K. Dimroth and F. Steuber, Angew. Chem., 79, 410 (1967).
194. C. Thomson and D. Kilcast, Chem. Comm., 1971, 214.
195. F. Jeffers, P. F. Wigen, and J. A. Cowen, Bull. Amer. Phys. Soc., 6, 118 (1961).

196. E. Hughes and W. G. Moulton, J. Chem. Phys., 39, 1359 (1963).
197. S. Subramanian, M. C. R. Symons, and H. W. Wardale, J. Chem. Soc. (A), 1970, 1239.
198. H. Lozykowski, R. C. Wilson, and F. Holuj, J. Chem. Phys., 51, 2309 (1969).
199. M. C. R. Symons, J. Chem. Phys., 53, 857 (1970).
200. F. Holuj, J. Chem. Phys., 54, 1430 (1971).
201. T. Gillbro and F. Williams, J. Amer. Chem. Soc., 96, 5032 (1974).
202. A. K. Hoffmann and A. G. Tesch, J. Amer. Chem. Soc., 81, 5519 (1959).
203. F. Hein and H. Hecker, Chem. Ber., 93, 1339 (1960).
204. Ya. A. Levin, Yu. M. Kargin, V. S. Galeev, and V. I. Sannikova, Izv. Akad. Nauk SSSR, Ser. Khim., 1968, 411.
205. A. V. Il'yasov, Yu. M. Kargin, Ya. A. Levin, B. M. Mel'nikov, and V. I. Galeev, Izv. Akad. Nauk SSSR, Ser. Khim., 1968, 2841.
206. S. P. Solodovnikov and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 2114.
207. S. P. Solodovnikov and M. I. Kabachnik, Teor. Eksper. Khim., 8, 518 (1972).
208. A. H. Cowley and M. H. Hnoosh, J. Amer. Chem. Soc., 88, 2585 (1966).
209. B. Allen and A. Bond, J. Phys. Chem., 68, 2439 (1964).
210. W. M. Gulick and D. H. Geske, J. Amer. Chem. Soc., 88, 2928 (1966).
211. W. M. Gulick, J. Amer. Chem. Soc., 94, 29 (1972).
212. G. Lassmann, W. Damerau, K. -H. Lohs, N. Klimes, and Z. Baldjeva, Z. Chem., 10, 297 (1970).
213. M. C. R. Symons, Mol. Phys., 24, 885 (1972).
214. M. C. R. Symons, Mol. Phys., 27, 785 (1974).
215. S. P. Mishra and M. C. R. Symons, Tetrahedron 1973, 4061.
216. S. P. Mishra and M. C. R. Symons, J. Chem. Soc. Dalton, 1973, 1494.
217. S. P. Mishra and M. C. R. Symons, J. Chem. Soc. Comm., 1974, 606.
218. V. V. Pen'kovskii, B. N. Kuz'minskii, Yu. P. Egorov, I. N. Zhmurova, and A. P. Martynyuk, Teor. Eksper. Khim., 6, 94 (1970).
219. V. V. Pen'kovskii, Yu. P. Egorov, I. N. Zhmurova, B. N. Kuz'minskii, and R. I. Yurchenko, Teor. Eksper. Khim., 6, 819 (1970).
220. V. V. Pen'kovskii, Yu. P. Egorov, I. N. Zhmurova, A. P. Martynyuk, and A. K. Shurubura, Teor. Eksper. Khim., 9, 112 (1973).
221. V. V. Pen'kovskii, Yu. P. Egorov, and G. S. Shapoval, Zhur. Obsch. Khim., 41, 738 (1971).
222. Yu. P. Egorov, V. V. Pen'kovskii, and B. N. Kuz'minskii, Teor. Eksper. Khim., 7, 601 (1971).
223. H. R. Allcock and W. J. Birdsall, J. Amer. Chem. Soc., 91, 7541 (1969).
224. S. P. Mishra and M. C. R. Symons, Chem. Comm., 1973, 313.
225. S. P. Mishra and M. C. R. Symons, Chem. Comm., 1974, 279.

Institute of Organic Chemistry,
Academy of Sciences of Ukrainian SSR, Kiev