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**Electron Spin Resonance Study of Phosphoranyl Radicals in  $\gamma$ -irradiated  $C_6H_5PCl_2$  and  $(C_6H_5)_2PCl$ .**

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Electron spin resonance (ESR) spectra of  $\gamma$ -irradiated  $C_6H_5PCl_2$  and  $(C_6H_5)_2PCl$  have showed clear features of phenylchlorophosphoranyl radicals. Phosphoranyl radicals have been extensively studied by ESR,<sup>1-6</sup> but ESR spectrum of phosphoranyl radical with phenyl substituent has not been reported. The present note describes the identification and some features of phenylchlorophosphoranyl radicals.

Samples of  $C_6H_5PCl_2$  and  $(C_6H_5)_2PCl$  were irradiated at 77°K in a <sup>60</sup>Co source for 10 hours at a dose rate of 0.1 Mrad/h. ESR measurements were carried out at 77°K with JEOL 3BSX and PE-1X spectrometers.

Figure 1 shows the high and low-field components of a doublet ESR spectrum of a radical produced by  $\gamma$ -irradiation of  $C_6H_5PCl_2$ . This spectrum indicates clearly the presence of a single phosphorus nucleus very strongly coupled with the odd electron (1060 G) and two strongly coupled equivalent chlorine nuclei (53 G). It is widely accepted that phosphoranyl radicals have a trigonal bipyramidal structure with the half-occupied hybrid orbital in the equatorial plane and that the splitting constants of the two axial nuclei are much larger than those of the two equatorial nuclei.<sup>1-6</sup> The hyperfine splitting constants (h.f.s.c.) of tetrachlorophosphoranyl radical ( $\dot{P}Cl_4$ ), formed by  $\gamma$ -irradiation of  $PCl_3$ , were reported<sup>3</sup> as  $a(P)=1214$ ,  $a(Cl\text{ axial})=62$ , and  $a(Cl\text{ equatorial})=7.5$  G. In the analogy to the spectrum of this tetrachlorophosphoranyl radical and its radical formation, we have identified the present radical species as phenyltrichlorophosphoranyl radical ( $C_6H_5\dot{P}Cl_3$ ), in which two chlorine nuclei occupy the axial positions and

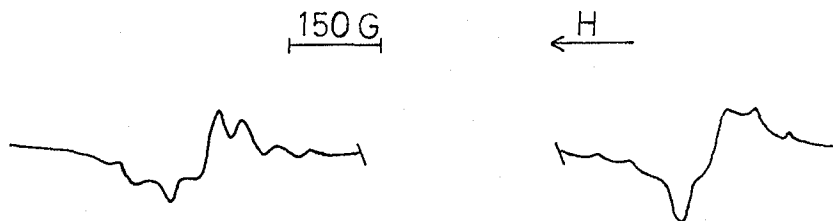


Fig. 1. ESR spectrum of  $C_6H_5\dot{P}Cl_3$  in  $\gamma$ -irradiated  $C_6H_5PCl_2$  at 77°K.

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Table I. ESR Parameters of  $C_6H_5\dot{P}Cl_3$ ,  $(C_6H_5)_2\dot{P}Cl_2$  and Some Related Radicals (G)

Radical	$g^a$	$a$ (P)	$a$ (Cl axial)	$\rho_{3s}(P)^b$
$\dot{P}Cl_4^c$	2.013	1214	62	0.33
$CH_3\dot{P}Cl_3^c$	2.000	1077	—	0.30
$C_6H_5\dot{P}Cl_3^d$	2.019	1060	53	0.29
$(C_6H_5)_2\dot{P}Cl_2^d$	2.014	813	59	0.22

<sup>a</sup> Corrected to second order with respect to the hyperfine interactions.

<sup>b</sup> Calculated from the Hartree-Fock value<sup>7</sup> of  $a_{3s}(P)=3640$  G.

<sup>c</sup> See Ref. 3.

<sup>d</sup> This work.

the third Cl nucleus and a phenyl ring occupy the equatorial positions, respectively.

Similarly, diphenyldichlorophosphoranyl radical ( $(C_6H_5)_2\dot{P}Cl_2$ ) with the two chlorine nuclei occupying the axial positions was observed in the ESR spectrum of  $\gamma$ -irradiated  $(C_6H_5)_2P\dot{C}l$ . The observed ESR parameters of these phosphoranyl radicals are presented in Table I together with some related radicals.

It is generally accepted that the s character of the unpaired electron orbital increases accompanying to the increase of electronegativity of ligand atoms.<sup>3)</sup> From this point of view, the data in Table I seems to be reasonable. Namely, the odd electron spin density on 3s atomic orbital of the phosphorus atom,  $\rho_{3s}(P)$ , decreases in the order of  $\dot{P}Cl_4$  (0.33),  $C_6H_5\dot{P}Cl_3$  (0.29),  $(C_6H_5)_2\dot{P}Cl_2$  (0.22) as shown in Table I. This fact offers further supports to the present identification of the radicals.

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