Note

Electron Spin Resonance Study of Phosphoranyl Radicals in γ-irradiated C₆H₅PCl₂ and (C₆H₅)₂PCl.

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Electron spin resonance (ESR) spectra of γ-irradiated C₆H₅PCl₂ and (C₆H₅)₂PCl have showed clear features of phenylchlorophosphoranyl radicals. Phosphoranyl radicals have been extensively studied by ESR,1-6) 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 C₆H₅PCl₂ and (C₆H₅)₂PCl were irradiated at 77°K in a 60Co 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 γ-irradiation of C₆H₅PCl₂. 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.1-6) The hyperfine splitting constants (h.f.s.c.) of tetrachlorophosphoranyl radical (PCl₄), formed by γ-irradiation of PCl₃, were reported3) as α(P)=1214, α(Cl axial)=62, and α(Cl 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 (C₆H₅PCl₃), in which two chlorine nuclei occupy the axial positions and

\[
\begin{align*}
150 \text{ G} \\
\end{align*}
\]

Fig. 1. ESR spectrum of C₆H₅PCl₃ in γ-irradiated C₆H₅PCl₂ at 77°K.

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Table I. ESR Parameters of C₆H₅PC₁₃, (C₆H₅)₂PC₁₂ and Some Related Radicals (G)

<table>
<thead>
<tr>
<th>Radical</th>
<th>g</th>
<th>a (P)</th>
<th>a (Cl axial)</th>
<th>ρ₃₉(P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC₁₄</td>
<td>2.013</td>
<td>1214</td>
<td>62</td>
<td>0.33</td>
</tr>
<tr>
<td>C₆H₅PC₁₃</td>
<td>2.000</td>
<td>1077</td>
<td>—</td>
<td>0.30</td>
</tr>
<tr>
<td>(C₆H₅)₂PC₁₂</td>
<td>2.019</td>
<td>1060</td>
<td>53</td>
<td>0.29</td>
</tr>
<tr>
<td>(C₆H₅)₂PC₁₄</td>
<td>2.014</td>
<td>813</td>
<td>59</td>
<td>0.22</td>
</tr>
</tbody>
</table>

a Corrected to second order with respect to the hyperfine interactions.
b Calculated from the Hartree-Fock value⁷ of ρ₃₉(P) = 3640 G.
c This work.

the third Cl nucleus and a phenyl ring occupy the equatorial positions, respectively.
Similarly, diphenyldichlorophosphoranyl radical ((C₆H₅)₂PC₁₂) with the two chlorine
nuclei occupying the axial positions was observed in the ESR spectrum of γ-irradiated
(C₆H₅)₂PC₁. 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.³ From this point
of view, the data in Table I seems to be reasonable. Namely, the odd electron spin density
on 3 s atomic orbital of the phosphorus atom, ρ₃₉(P), decreases in the order of PC₁₄ (0.33),
C₆H₅PC₁₃ (0.29), (C₆H₅)₂PC₁₂ (0.22) as shown in Table I. This fact offers further
supports to the present identification of the radicals.

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REFERENCES