Note

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

Takashi KAWAMURA, Tsukasa TADA, Yoshio SUGIYAMA, and Teijiro YONEZAWA*

Received December 16, 1974

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

\[ \text{Fig. 1. ESR spectrum of C}_6\text{H}_5\text{PCl}_3 \text{ in γ-irradiated C}_6\text{H}_5\text{PCl}_2 \text{ at 77°K.} \]
T. KAWAMURA, T. TADA, Y. SUGIYAMA, and T. YONEZAWA

Table I. ESR Parameters of C₆H₅PCl₄, (C₆H₅)₂PCl₂ and Some Related Radicals (G)

<table>
<thead>
<tr>
<th>Radical</th>
<th>g²⁰¹₃</th>
<th>a (P)</th>
<th>a (Cl axial)</th>
<th>p₃₈(P)²⁰³⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCl₄         c</td>
<td>2.013</td>
<td>1214</td>
<td>62</td>
<td>0.33</td>
</tr>
<tr>
<td>CH₃PCl₂      c</td>
<td>2.000</td>
<td>1077</td>
<td>—</td>
<td>0.30</td>
</tr>
<tr>
<td>C₆H₅PCl₃     d</td>
<td>2.019</td>
<td>1060</td>
<td>53</td>
<td>0.29</td>
</tr>
<tr>
<td>(C₆H₅)₂PCl₄   d</td>
<td>2.014</td>
<td>813</td>
<td>59</td>
<td>0.22</td>
</tr>
</tbody>
</table>

² Corrected to second order with respect to the hyperfine interactions.
²² Calculated from the Hartree-Fock value of a₂₧(P) = 3640 G.
³ See Ref. 3.
⁴ This work.

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

Similarly, diphenyldichlorophosphoranyl radical ((C₆H₅)₂PCl₂) with the two chlorine nuclei occupying the axial positions was observed in the ESR spectrum of γ-irradiated (C₆H₅)₂PCl. 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, p₃₈(P), decreases in the order of PCl₄ (0.33), C₆H₅PCl₃ (0.29), (C₆H₅)₂PCl₂ (0.22) as shown in Table I. This fact offers further supports to the present identification of the radicals.

ACKNOWLEDGMENTS

The authors are grateful to Professor S. Shimizu and Mr. R. Katano for giving them a chance to use the ⁶⁰Co γ-ray source.

REFERENCES