Single crystal ESR study of xirradiated thiophosphate O,O,O-triester of methyl Dribopyranoside: Electron capture by the thiophosphate moiety
Hamerlinck, J.H.H.; Schipper, P.; Buck, H.M.

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.443313

Published: 01/01/1982

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Single crystal ESR study of x-irradiated thiophosphate O,O,O-triester of methyl β-D-ribopyranoside: Electron capture by the thiophosphate moiety

J. H. H. Hamerlinck, P. Schipper, and H. M. Buck

Eindhoven University of Technology, Department of Organic Chemistry, The Netherlands
(Received 18 September 1981; accepted 17 November 1981)

X-irradiation of a single crystal of thiophosphate O,O,O-triester of methyl β-D-ribopyranoside at 77 K produces a σ phosphoranyl radical anion (2) by electron capture among secondary radicals resulting from bond scission. The ESR parameters of (2) in correlation with the x-ray analysis of its precursor establish a TBP structure with the unpaired electron in apical position. The results suggest that in irradiated nucleic acid polymers, electrons can be trapped by phosphorus giving rise to a phosphorus-centered radical which subsequently induces bond break by α or β scission generating thermodynamically more stable sugar and base radicals.

INTRODUCTION

The effects of ionizing radiation in living cells have been the subject of much recent research because the lethal damage is thought to be partially due to DNA strand breaks. The radical products have been studied by ESR. On comparison with model ESR studies on irradiated nucleosides and nucleotides, a variety of radicals have been assigned. It has been assumed that phosphorus σ radicals might be involved in reduction processes upon irradiation. Recently, the PO!- radical which is the product of C-O bond scission in γ-irradiated α-glycerophosphate, has been assigned with $\alpha_{P-O} = 30$ G, indicating an oxygen-centered radical. However, the involvement of a phosphorus-centered σ radical, i.e., a phosphoranyl or phosphoryl radical, has not been considered.

In this paper we report the occurrence of a phosphoranyl P' radical which is formed by electron capture upon x-irradiation of thiophosphate O,O,O-triester of methyl β-D-ribopyranoside.

EXPERIMENTAL SECTION

Single crystals of the thiophosphate O,O,O-triester of methyl β-D-ribopyranoside (1) which are grown by slow crystallization from (diethyl)ether, are orthorhombic with space group $P_{2_1}2_12_1$ with four molecules in a unit cell (Fig. 1). Crystal alignment was performed by use of a polarization microscope. From the extinction curve the directions of the crystallographic axes were obtained. These axes were easily identified by means of the rotating-crystal method, using CuKα radiation. The radical was generated by x-irradiation at 77 K. Irradiated crystals, glued on a small quartz rod, were studied at 203 K on a Varian E-4 ESR spectrometer equipped with a single axis goniometer.

RESULTS

X-irradiation at 77 K of a single crystal of (1) gives rise to the ESR spectrum assigned to (2). The other (central) features, which are analogous to those reported for comparable sugar radicals, are not analyzed here.

The concentration of (2) is increased by raising the temperature, reaching an optimum at 203 K, while its ESR signal disappeared at about 243 K. The ESR spectrum of (2) consists of two sets of $^{31}$P doublets, each set possessing one $^1$H coupling. The angular variations are shown in Figs. 2(a) and 2(b). On rotation about the crystallographic c axis, two identical
radicals with an angle between their $a_{p\|}$ components of $60^\circ \pm 2^\circ$ are present [Fig. 2(a)]. Upon rotation around the crystallographic $b$ axis only one site was detected [Fig. 2(b)]. Furthermore, the $a_p$ value obtained from Fig. 2(a) along the crystallographic $a$ axis equals that found from Fig. 2(b) along the same axis. From this it is concluded that the $a_{p\|}$ components of both sites are located in the $ab$ plane. The $^1H$ coupling appears to be isotropic. The ESR parameters are collected in Table I.

**ASSIGNMENT**

The directions of the $a_{p\|}$ components fit excellently into the stereo projection of the unit cell along the $c$ axis upon the $ab$ plane (Fig. 3). The projections of the $P-O_2$ linkages in this plane make angles of $56^\circ$. Therefore, we indicate the direction of the $a_{p\|}$ components as shown in Fig. 3. Furthermore, the $P-O_2$ linkages make an angle of $108^\circ$ (or supplementary) with

![FIG. 2. (a) Angular variation of $a_p$ in the $ab$ plane. (b) Angular variation of $a_p$ in the $ac$ plane.](image)

![FIG. 3. Projection of the unit cell of (1) along the $c$ axis, the location of the unpaired electron is indicated.](image)

**TABLE I. ESR parameters and spin densities for (2).**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{e|}$</td>
<td>886</td>
</tr>
<tr>
<td>$a_{e\perp}$</td>
<td>776</td>
</tr>
<tr>
<td>$a_{1p|}$</td>
<td>813</td>
</tr>
<tr>
<td>$B$</td>
<td>37</td>
</tr>
<tr>
<td>$\rho_{P}$</td>
<td>0.22</td>
</tr>
<tr>
<td>$\rho_{P3}$</td>
<td>0.35</td>
</tr>
<tr>
<td>$^1H$</td>
<td>5</td>
</tr>
<tr>
<td>$g$</td>
<td>1.988</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>2.005</td>
</tr>
</tbody>
</table>


Downloaded 05 Sep 2011 to 131.155.2.66. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions
the crystallographic c axis. Thus, the structure of (2)
has to be described as trigonal bipyramidal (TBP) with the
O₂ oxygen ligand and the unpaired electron in the
apical positions, the O₂-P- angle being 162°, while the
O₃-P-S angle probably will decrease from 121° to
90°. From the anisotropic values of the phosphorus
hyperfine coupling constants aₚ = 886 G and aₚ₁ = 776 G,
the aₚiso is calculated² to be 813 G. These values indi-
cate a phosphorus 3s spin density of 0.22 and a 3p
spin density of 0.35, resulting in a total spin density
of 0.57 located on phosphorus in apical position.

The hfc of 5 G can be ascribed to the hydrogen in
quasiapical position C₁-H, vide infra, which value has
probably a negative sign, because it is the result of
spin polarization in accordance with its isotropic char-
acter. The quasiapical C₂-H and C₃-H hydrogen
hfc are not observed. The remaining spin density will
be distributed over the equatorial ligands O₁, O₃,
and S.

**DISCUSSION**

The possibility that the ESR spectra described above
have to be attributed to a radical which would be the
result of scission of the P-O₂ bond, i.e., a phosphonyl
radical, is ruled out on the basis of its aₚ values, in
the case of, e.g., (MeO)₂P=O an aₚiso = 700 G, has
been observed.¹⁰ Furthermore, in the latter type of
radical two equivalent ¹H splittings would have been
observed.

The assignment of the small ¹H hfc to the C₂-H hydro-
gen is consistent with the results of other TBP P⁷⁺ radicals which also show a unique hydrogen splitting of 3-7 G for the hydrogen id quasiapical position and zero hfc for pseudoquatorial hydrogens.¹¹ In fact, the unique splitting of 5 G is similar to that we found for the hydrogen in the structurally related radical (3) which is formed in liquid phase by photolysis of di-t-
butylperoxide in the presence of phosphite (4), showing
aₚiso = 895 G and aₚ = 7 G (1H).

\[ \text{BuOOBu} \rightarrow \text{P=O} \]

The TBP-α configuration found for (2) agrees with the
\[ \text{P(OC₂H₅)}₂N°\text{BF₄}^- \] radical (5),¹² which adopts a
TBP-α structure with the unpaired electron and nitrogen
in the apical positions, the N-P- angle being 168°. Also its ³¹P hfc values are almost identical,
aₚ = 888 G, aₚ₁ = 753 G, and an additional ¹⁴N hfc aₙ₁ = 21.2 G, aₙ₂ = 22.7 G.

Obviously, radical (2) has been generated by elec-
tron capture at phosphorus. Its TBP structure will be
stabilized by the two five-membered rings which span
apical-equatorial positions, placing the six-membered
ring diequatorially.¹³ Electronically, it is conceivable
that the negative sulfur ligand favors the equatorial
position in this rigid frame work.

On warming, the ESR signal disappeared at -30°C
indicating α or β scission which processes are known
to occur readily in P⁷⁺ radicals,¹⁴ giving rise to rela-
tively stable sugar radicals.

In the absence of the P⁷⁺ stabilizing factors α or β
scission may occur in such rate that the P⁷⁺ structure
cannot be detected. For example, in irradiated de-
oxoyctidine-5'-phosphate (8) the radical (7) has been
observed.¹⁵ We propose here that this radical
probably will be the result of β scission of the inter-

\[ \text{K} \]

mediate phosphorus-centered σ radical which is formed
by electron capture. In nucleic acid polymers this type
of scission gives rise to strand breaks, indicating its
importance for the living cell.

**ACKNOWLEDGMENTS**

This investigation has been supported by the Nether-
lands Foundation for Chemical Research (SON) with
financial aid from the Netherlands Organization for the
Advancement of Pure Research (ZWO). We thank
Mr. H. Eding for the drawings.

¹M. Dizdaroglu, C. von Sonntag, and D. Schulte-Frohlinde,
³Thiophosphate O₁O₃O-triester of methyl β-D-ribopyranoside
(1) was a gift from Dr. A. C. Bellaart, Department of Organic
Chemistry, Eindhoven University of Technology, The Nether-
lands.
⁴A. C. Bellaart, D. van Aken, H. M. Buck, C. H. Stam, and
The ORTEP drawings were kindly delivered by Dr. G. J. Visser, Computing Centre of the Eindhoven University of Technology, The Netherlands.