Irradiation Damage Centers in Magnesiumhypophosphite

F. Köksal and H. Yüksel

Department of Physics, Faculty of Science, Ankara University

(Z. Naturforsch. **30 a**, 1044–1048 [1975]; received May 5, 1975)

An analysis of the electron spin resonance spectra of gamma-irradiated crystals of magnesium-hypophosphite, $Mg(H_2PO_2)_2 \cdot 6\,H_2O$, has shown that the main long-lived paramagnetic species produced by gamma-irradiation are HPO_2^- and $PO_3^=$ ionic radicals. The hyperfine interaction tensor of the phosphorous nucleus has the principal values $T_{||}=1674$, $T_\perp=1221$ Mc/s in HPO_2^- and $T_{||}=2490$, $T_\perp=1847$ Mc/s in $PO_3^=$. In HPO_2^-, interaction of the unpaired electron with the proton gives rise to an almost isotropic hyperfine coupling of 233 Mc/s. These results indicate that the orbitals occupied by the unpaired electron in both HPO_2^- and $PO_3^=$ are sp^3-hybrid σ-orbitals centered on the phosphorous nuclei.

1. Introduction

It is known in many cases that C – H bonds are broken by the action of high energy gamma rays on solids. One of the simplest example is the formate ion HCO_2^- in which hydrogen is driven away giving the CO_2^- ionic radical [1]. On the other hand, the same thing happens in inorganic substances giving two, three, tetra and penta atomic ionic radicals [2, 3]. In ammonium hypophosphite, $NH_4H_2PO_2$, gamma irradiation produces HPO_2^- radicals [4], and in magnesium phosphite, $MgHPO_3 \cdot 6\,H_2O$, x-ray irradiation produces $PO_3^=$ radicals [5]. Therefore it seemed of interest to see what kind of species occur in $Mg(H_2PO_2)_2 \cdot 6\,H_2O$. Consequently, the electron spin resonance spectrum of gamma irradiated magnesium hypophosphite hexahydrate single crystal was investigated to see if hydrogen could be removed from the $H_2PO_2^-$ ion to give the ionic radical HPO_2^- and it some other ionic species such as $PO_3^=$ occur.

2. Experimental Details

Crystal of magnesium hypophosphite hexahydrate were grown from equeus solution and irradiated at room temperature with a Cobalt-60 gamma-ray source (250 c) for 24 hours. The morphology of the crystals with the crystal axes is shown in Figure 1. The unit cell has tetragonal symmetry and contains 8 molecules. The symmetry was confirmed with x-ray diffraction experiments. The spectra of the irradiated crystals were obtained with a Varian X-band E-line ESR spectrometer with a 15″ magnet at the Hacettepe University of Ankara. The

Reprint requests to Dr. F. Köksal, A. Ü. Fen Fakültesi, Fizik Bölümü, Turkey.

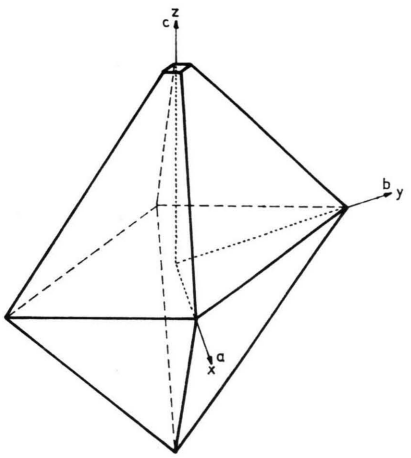


Fig. 1. Morphology of $Mg(H_2PO_2)_2 \cdot 6\,H_2O$ crystal, showing unit cell directions.

crystals were rotated about each of the axes in turn and the spectra were recorded at intervals of 15° using 2 mW microwave pover. The axis of rotation was kept perpendicular to the main magnetic field.

3. Description of ESR Spectra

The spectrum obtained from a gamma-irradiated crystal of $Mg(H_2PO_2)_2 \cdot 6\,H_2O$ when the magnetic field is paralel to one of the three crystallographic axes consists of four sharp lines with two small lines symmetrically located at both sides as shown in Figure 2. When the microwave power is increased, these two lines become stronger while the four-line pattern becomes weaker in intensity. In addition, there appear several lines in the middle of the spectrum which we shall not consider in this paper. The four-line spectrum obtained for the field along a crystallographic axis indicates a hyperfine interaction with two nuclei of spin 1/2. For these par-

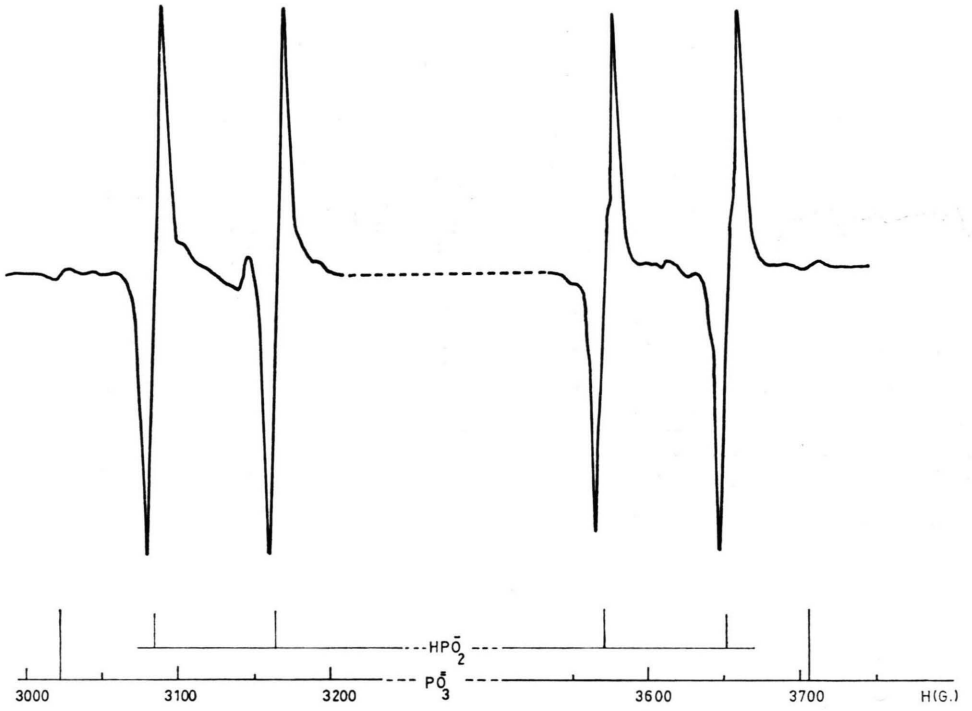


Fig. 2. Derivative spectrum of an irradiated single crystal of magnesium hypophosphite, H parallel to a-axis.

ticular orientations the spectra of all sites superimpose exactly. However, when the magnetic field explores the ab, bc or ac planes, distinguishable sites are observed. If the magnetic field does 65° and 105° with the y-axis in the xy-plane then, due to two and three magnetically different sites, 8 and 12-line patterns (Figures 3 a and 3 b) are obtained, respectively. In the last case the number of species in the three sites should be 4, 8 and 4. We obtain 64 almost resolved lines in the skew orientation showing the presence of sixteen HPO_2^- radicals in the unit cell, which is in agreement with the unit cell properties of the crystal[6]. HPO_2^- occurs by losing a hydrogen atom from $H_2PO_2^-$.

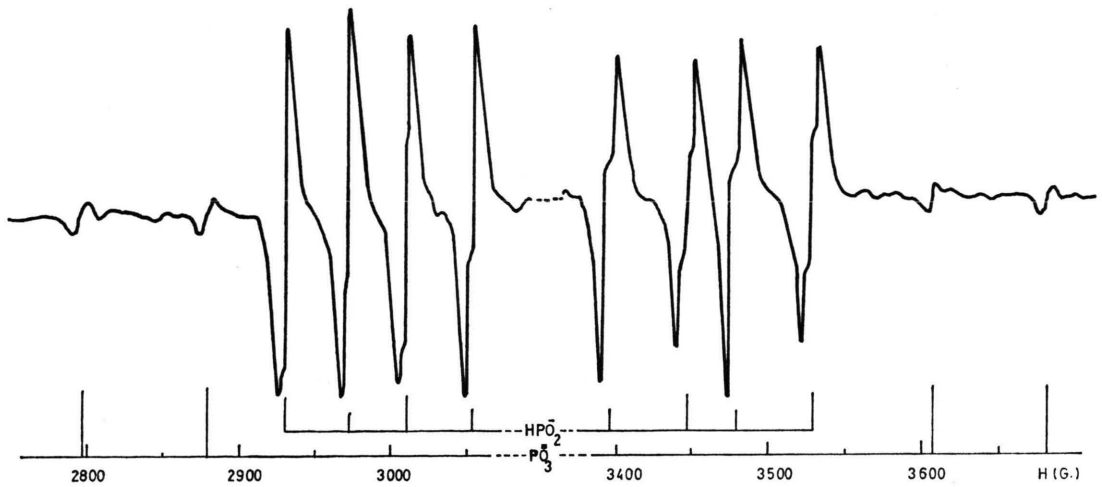
The very small two-line spectrum mentioned above doubles and becomes a sixteen-line spectrum when the magnetic field explores the above mentioned planes. This spectrum is attributed to $PO_3^=$ radicals.

4. Determination of g and Hyperfine Interaction Tensors

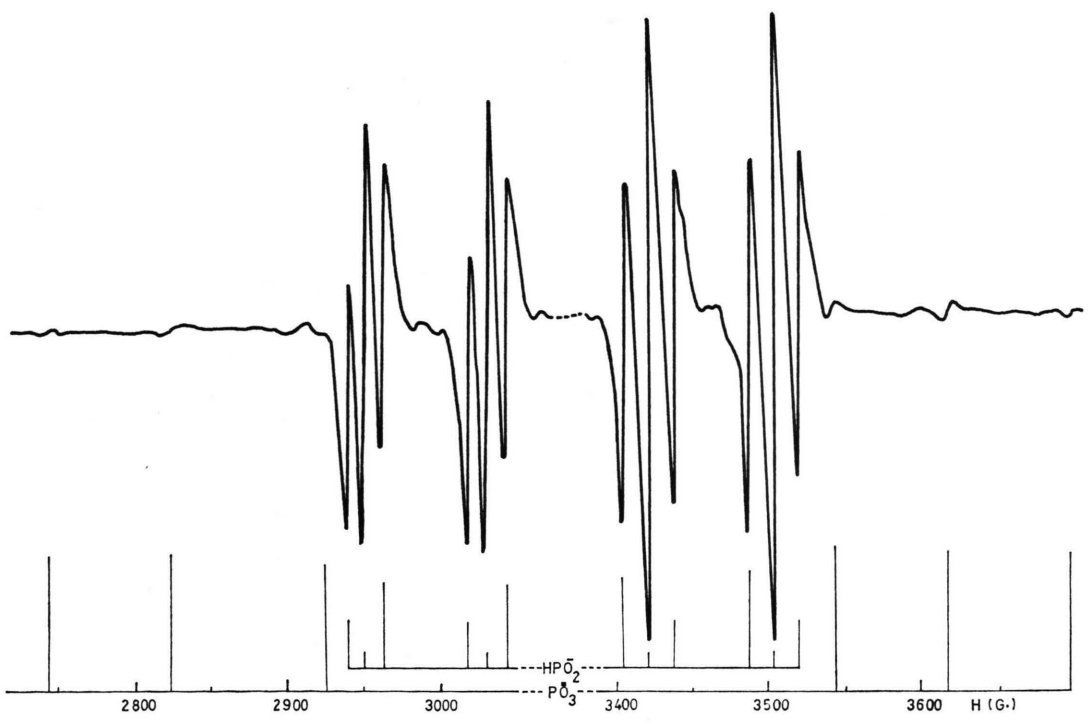
It is seen from Table 3 that the hyperfine splitting of the P^{31} nucleus is exceedingly large. Therefore the electron spin can not be assumed to be quantized along the magnetic field direction and terms of second order in the hyperfine interaction of the nucleus with the unpaired electron must be retained in the Hamiltonian. In this case it is easier to evaluate the problem in the principal axis system which diagonalizes both the g tensor and the P^{31} hyperfine interaction tensor, T. When the magnetic field is along the z-axis the simplified Hamiltonian

$$\mathcal{H} = \beta S_z g_{zz} H_z - \gamma I_{zz} H_z + S_x T_{xx} I_x + S_y T_{yy} I_y + S_z T_{zz} I_z \qquad (1)$$

is used, where β is the Bohr magneton and γ the magnetogyric ratio of the P^{31} nucleus. If S_x and S_y are non zero, the electron spin is not quantized along the z-axis and some mixing of certain electron spin states occurs. To evaluate this case, the matrix representation of the Hamiltonian in Eq. (1) is written on the basis of $|++>$, $|-->$, $|+->$, $|-+>$ where the first signs indicate the eigenvalues of S_z and the second signs indicate the eigenvalues of I_z. + signs stay tor 1/2 and − signs for −1/2. In this case the secular equation factorizes into two quadratics. The eigenvalues and the eigenfunctions are given in Table 1. When the spectrum



3 a



3 b

Fig. 3. Spectra of irradiated $Mg(H_2PO_2)_2 \cdot 6\,H_2O$ single crystal. 3 a) H is in the xy-plane and it does 65° with the y-axis, 3 b) H does 105° with the y-axis in the xy-plane.

is observed at constant microwave frequency it may be shown that

$$\nu = g_{zz}\beta H_z^- + \tfrac{1}{2}T_{zz} + (T_{zz}^2 + T_{yy}^2)/8\,g_{zz}\beta H_z^- \quad (2)$$

for the low-field line at H_z^- gauss and

$$\nu = g_{zz}\beta H_z^{\pm} \mp \tfrac{1}{2}T_{zz} + (T_{xx}^2 + T_{yy}^2)/8\,g_{zz}\beta H_z^+ \quad (3)$$

for the high-field line at H_z^+ gauss. The corresponding equations for H parallel to x and y are obtained by making cyclic permutations in the subscripts. In our case, since there is axial symmetry, $T_{zz} = T_{\parallel}$ and $T_{yy} = T_{xx} = T_{\perp}$. The same subscripts are valid for the g tensor. Under these conditions

Table 1. Energy levels, wave functions and the low and the high field transition frequencies when the magnetic field is parallel to a principal axis of g and T.

Levels	Energy	Wave functions	Transition energies
$\|++>$	$\frac{T_{zz}+U}{4}$	$\cos\Phi\|++>+\sin\Phi\|-->$	$\|++>\longleftrightarrow\|-+>$ Low field
$\|-->$	$\frac{T_{zz}-U}{4}$	$-\sin\Phi\|++>+\cos\Phi\|-->$	$\frac{2T_{zz}+W+U}{4}$
$\|+->$	$\frac{-T_{zz}+W}{4}$	$\cos\theta\|+->+\sin\theta\|-+>$	$\|-->\longleftrightarrow\|+->$ High field
$\|-+>$	$\frac{-T_{zz}-W}{4}$	$-\sin\theta\|+->+\cos\theta\|-+>$	$\frac{2T_{zz}-U+W}{4}$

Where: $U^2=4H^2(g_{zz}\beta-g_N\beta_N)^2+(T_{zz}-T_{yy})^2$ Tan $2\Phi=(T_{zz}-T_{yy})/2H(g_{zz}\beta-g_N\beta_N)$

$W^2=4H^2(g_{zz}\beta+g_N\beta_N)^2+(T_{zz}+T_{yy})^2$ Tan $2\theta=(T_{zz}+T_{yy})/2H(g_{zz}\beta+g_N\beta_N)$

the four equations which can be solved iteratively for $T_{\|}$, $T_{\perp}$, $g_{\|}$ and $g_{\perp}$ are for the parallel orientation,

$$\nu_{\|}=(g_{\|}\beta-g_N\beta_N)H^{\pm}\mp\tfrac{1}{2}T_{\|}+\frac{T_{\perp}^2}{4(g_{\|}\beta-g_N\beta_N)H^{\pm}} \quad (4)$$

and for the perpendicular orientation,

$$\nu_{\perp}=(g_{\perp}\beta-g_N\beta_N)H^{\pm}\mp\tfrac{1}{2}T_{\perp}+\frac{T_{\|}^2+T_{\perp}^2}{8(g_{\perp}\beta-g_N\beta_N)H^{\pm}} \quad (5)$$

With the aid of these equations and the experimental data in Table 2 the principal values of the g tensor and the P^{31} hyperfine interaction tensors for the radicals HPO_2^- and $PO_3^=$ were determined.

Table 2. ESR field strengths (Gauss) of HPO_2^- and $PO_3^=$ radicals in gamma irradiated $Mg(H_2PO_2)_2\cdot 6H_2O$ crystal.

Radical	Parallel orientation (G)		Perpenticular orientation (G)	
	$H_{\|}^-$	$H_{\|}^+$	$H_{\perp}^-$	$H_{\perp}^+$
HPO_2^-	3080	3680	3015	3453
$PO_3^=$	2920	3820	2880	3550
Microwave frequency (Mc/s)	9509		9135	

5. Results and Discussion

The proton hyperfine interaction tensor in HPO_2^- was nearly isotropic within the limits of experimental errors. Evaluation of its value was straightforward with the result of 233 Mc/s. The nucleus responsible for the largest coupling is obviously phosphorous. The obtained values of g and the hyperfine interaction tensors for both HPO_2^- and $PO_3^=$ are given in Table 3. The quantities $T_{\|}$ and $T_{\perp}$ are of special interest because they give information about the electronic structure of the paramagnetic species. These quantities are the sum of two parts, the isotropic and the anisotropic interactions. In HPO_2^- the isotropic part of T is 1372 and the dipolar parts are $T_{d\|}=302$, $T_{d\perp}=-151$ Mc/s. The same quantities for $PO_3^=$ are $T_{iso.}=2061$, $T_{d\|}=429$, $T_{d\perp}=-215$. The extremely large values of isotropic hyperfine interactions observed in this study indicate that there is a direct mechanism for getting the unpaired electron density at the nucleus. Therefore the orbital occupied by the unpaired electron must be a hybrid orbital containing considerable s-character. Actually the orbitals occupied by the unpaired electrons in both cases of HPO_2^- and $PO_3^=$ are sp^3 hybrid σ-orbitals. From the S.C.F.

Table 3. Principal values and direction cosines of g and hyperfine interaction tensors of the P^{31} nucleus in HPO_2^- and $PO_3^=$ radicals.

Radical	$g_{\|}$	$g_{\perp}$	$T_{\|}$ (Mc/s)	$T_{\perp}$ (Mc/s)
HPO_2^-	2.0029	2.0061	1674	1221
	(0.00, −0.70, 0.70)	(−0.70, 0.70, 0.00)	(0.00, −0.70, 0.70)	(−0.70, 0.70, 0.00)
$PO_3^=$	1.9977	2.0013	2490	1847
	(0.00, −0.17, 0.99)	(0.96, −0.42, 0.00)	(0.00, −0.17, 0.99)	(0.96, −0.42, 0.00)

wave functions of Watson and Freeman [7] a value of $\Psi^2(0) = 5.634$ A.U.$^{-3}$ may be estimated for the 3s orbital of the phosphorous atom. This corresponds to an isotropic hyperfine coupling of an electron to the P^{31} nucleus of $(8\pi/3) g \beta g_N \beta_N \Psi^2(0) = 10180$ Mc/s. The observed isotropic coupling to the P^{31} nucleus of 1372 Mc/s corresponds to 13.5 per cent 3s-character. Similarly, by using Watson and Freeman's wave function the average value of r^{-3} for the 3p-orbital of phosphorous was found to be 3.32 A.U.$^{-3}$, and this gives $(4 g \beta g_N \beta_N / 4h) \langle r^{-3} \rangle_{av.} =$ 574 Mc/s pure 3p-orbital contribution. So the experimentally observed 302 Mc/s corresponds to a spin population of 0.525. Finally, the isotropic proton hyperfine interaction of 233 Mc/s corresponds to 16.4 per cent spin population in the hydrogen 1s-orbital. Consequently there is left 8.8 per cent spin population on each oxygen.

By using the above numeric values for the P^{31} nucleus we find 20 per cent 3s and 75 per cent 3p spin population on $P^{3'}$ nucleus in $PO_3^=$. So there is left only 1.7 per cent spin population on each oxygen. Hence we obtain hybridisation ratios $\lambda = (C_p^2/C_s^2)^{1/2}$ for both HPO_2^- and $PO_3^=$ and estimate the OPO bond angles by using Coulson's relation [8],

$$\Phi = \cos^{-1}\left[\frac{1.5}{2\lambda^2+3} - \frac{1}{2}\right].$$

The results are 111.2° for HPO_2^- and 110.9° for $PO_3^=$. They show that the first radical is somewhat closer to planarity than the latter. The large values of hydrogen hyperfine interaction in HPO_2^- can be explained by using Morton's [4] and Adrian et al.'s [9] arguments. The half life (24 hours) for the radical HPO_2^- reported by Morton [4] was more than two months in our case and this suggests that life-times of trapped radicals change according to crystals. Finally, comparison of our g and hyperfine tensors for the radicals HPO_2^- and $PO_3^=$ with several authors, Table 4, shows that, although they may live different lengths of times, their g and T values do not show large differences.

Acknowledgement

The authors wish to thank Dr. M. Korkmaz and Dr. A. Gedikoğlu for their assistance in preparing this work.

Table 4. Principal values of g and T tensors for HPO_2^- and $PO_3^=$ radicals.

Parent crystal	Radical	$g_{\|\|}$	$g_\perp$	$T_{\|\|}$ (Mc/s)	$T_\perp$ (Mc/s)	Reference
$NH_4H_2PO_2$	HPO_2^-	2.0019	2.0037	1698	1228	[4]
$Mg(H_2PO_2)_2 \cdot 6\,H_2O$	HPO_2^-	2.0029	2.0061	1674	1221	Present work
$Na_2HPO_3 \cdot 5\,H_2O$	$PO_3^=$	1.9994	2.0011	1967	1514–1513	[10]
$MgHPO_3 \cdot 6\,H_2O$	$PO_3^=$	1.998	1.999	2210	1730	[5]
$(NH_4)_2H_2P_2O_6$	$PO_3^=$	2.0000	2.0012	2420	1960–1940	[11]
$(NH_4)_2HPO_4$	$PO_3^=$			2070	1600	[12]
$(NH_4)_2PO_3F \cdot H_2O$	$PO_3^=$	1.9994	2.0011	1822	1420–1409	[13]
$Na_2DPO_3 \cdot 5\,D_2O$	$PO_3^=$			1963	1680	[14]
$Mg(H_2PO_2)_2 \cdot 6\,H_2O$	$PO_3^=$	1.9977	2.0013	2490	1847	Present work

[1] D. W. Ovenall and D. H. Whiffen, Mol. Phys. **4**, 135 [1961].
[2] M. C. R. Symons and P. W. Atkins, The Structure of Inorganic Radicals, Elsevier, London 1968.
[3] J. R. Morton, Chem. Rev. **64**, 453 [1964].
[4] J. R. Morton, Mol. Phys. **5**, 217 [1962].
[5] M. W. Hanna and L. R. Altman, J. Chem. Phys. **36**, 1788 [1962].
[6] A. R. Pedrazuela, S. Garcia-Blanco, and L. Rivor, Anales rel Soc. espan. fils. y quim, Madrid **49 A**, 255 [1953].
[7] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 521 [1961].
[8] C. A. Coulson, Volume Commémoratit Victor Henri, Contributions d l'Etude de la structure Moléculaire, 1948, p. 15.
[9] F. J. Adrian, E. L. Cochran, and V. A. Bowers, J. Chem. Phys. **36**, 1661 [1962].
[10] A. Horsfield, J. R. Morton, and D. H. Whiffen, Mol. Phys. **4**, 475 [1961].
[11] J. R. Morton, Mol. Phys. **6**, 193 [1963].
[12] J. R. Morton, J. Phys. Chem. Sol. **24**, 209 [1963].
[13] F. G. Herring, J. H. Hwang, W. C. Lin, and C. A. Mc Dowell, J. Phys. Chem. **70**, 2487 [1966].
[14] S. Schlick, B. L. Silver, and Z. Luz, J. Chem. Phys. **52**, 1232 [1969].