An analysis of the electron spin resonance spectra of gamma-irradiated crystals of magnesium-hypophosphite, Mg(HPO₄)₂·6H₂O, has shown that the main long-lived paramagnetic species produced by gamma-irradiation are HPO₄⁻ and PO₄³⁻ ionic radicals. The hyperfine interaction tensor of the phosphorous nucleus has the principal values $T_{11} = 1674$, $T_{12} = 1221$ Mc/s in HPO₄⁻ and $T_{11} = 2490$, $T_{12} = 1847$ Mc/s in PO₄³⁻. In HPO₄⁻, 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 HPO₄⁻ and PO₄³⁻ are sp³-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 CO₂⁻ ionic radical. On the other hand, the same thing happens in inorganic substances giving two, three, tetra and penta atomic ionic radicals. In ammonium hypophosphite, NH₄H₂PO₄, gamma irradiation produces HPO₄⁻ radicals, and in magnesium phosphite, MgHPO₄·6H₂O, x-ray irradiation produces PO₄³⁻ radicals. Therefore it seemed of interest to see what kind of species occur in Mg(H₂PO₄)₂·6H₂O. 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 H₃PO₄⁻ ion to give the ionic radical HPO₄⁻ and if some other ionic species such as PO₄³⁻ 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 crystals were rotated about each of the axes in turn and the spectra were recorded at intervals of 15° using 2 mW microwave power. 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(H₂PO₄)₂·6H₂O when the magnetic field is parallel 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-
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$_2$PO$_4^-$. 

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

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

is used, where $\beta$ is the Bohr magneton and $\gamma$ the magnetogyrar 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.

Fig. 2. Derivative spectrum of an irradiated single crystal of magnesium hypophosphite, $H$ parallel to $a$-axis.
is observed at constant microwave frequency it may be shown that

\[ \nu = g_{zz} \beta H_z^- + \frac{1}{2} T_{zz} + (T_{xx}^2 + T_{yy}^2) / 8 g_{zz} \beta H_z^- \]  \hspace{0.5cm} (2)

for the low-field line at \( H_z^- \) gauss and

\[ \nu = g_{zz} \beta H_z^+ + \frac{1}{2} T_{zz} + (T_{xx}^2 + T_{yy}^2) / 8 g_{zz} \beta H_z^+ \]  \hspace{0.5cm} (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, \( T_{zz} = T_{||} \) and \( T_{yy} = T_{xx} = T_{\perp} \). The same subscripts are valid for the \( g \) tensor. Under these conditions
the four equations which can be solved iteratively for $T_\parallel$, $T_\perp$, $g_\parallel$ and $g_\perp$ are for the parallel orientation,
\[ v_\parallel = (g_\parallel \beta - g_N \beta_N) H_\parallel^z \mp \frac{1}{2} T_\parallel + \frac{T_\parallel^2}{4(g_\parallel \beta - g_N \beta_N) H_\parallel^z} \]
and for the perpendicular orientation,
\[ v_\perp = (g_\perp \beta - g_N \beta_N) H_\perp^z \mp \frac{1}{2} T_\perp + \frac{T_\perp^2}{8(g_\perp \beta - g_N \beta_N) H_\perp^z} \]

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($H_2PO_2$)$2\cdot6H_2O$ crystal.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Parallel orientation (G)</th>
<th>Perpendicular orientation (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HPO_2^-$</td>
<td>$H_\parallel$</td>
<td>$H_\perp$</td>
</tr>
<tr>
<td></td>
<td>3080</td>
<td>3680</td>
</tr>
<tr>
<td>$PO_3^-$</td>
<td>2920</td>
<td>3820</td>
</tr>
<tr>
<td>Microwave frequency (Mc/s)</td>
<td>9509</td>
<td>9135</td>
</tr>
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</table>

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 $T_\parallel$ 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 $T_{\parallel}=302$, $T_{\perp}=-151$ Mc/s. The same quantities for $PO_3^-$ are $T_{\parallel}=2061$, $T_{\perp}=2490$, $T_{\parallel}=1847$. 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 $\sigma$-orbitals. From the S.C.F.
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 \((4g\beta g_N\beta_N/4\hbar)(r^{-3})_{av.} = 574\) 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 ls-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 \(P^{31}\) nucleus in \(PO_3^-\). So there is left only 1.7 per cent spin population on each oxygen. Hence we obtain hybridisation ratios \(\lambda = (C_s^2/C_p^2)^{1/3}\) for both \(HPO_2^-\) and \(PO_3^-\) and estimate the OPO bond angles by using Coulson’s relation\(^8\).

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

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. Gedikoglu for their assistance in preparing this work.

<table>
<thead>
<tr>
<th>Parent crystal</th>
<th>Radical</th>
<th>(g_{\parallel})</th>
<th>(g_{\perp})</th>
<th>(T_{\parallel}) (Mc/s)</th>
<th>(T_{\perp}) (Mc/s)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>(NH_2HPO_3)</td>
<td>(HPO_2^-)</td>
<td>2.0019</td>
<td>2.0037</td>
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<td>1228</td>
<td>Present work</td>
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<tr>
<td>(Mg(H_2PO_4)_2\cdot 6 H_2O)</td>
<td>(HPO_2^-)</td>
<td>2.0029</td>
<td>2.0061</td>
<td>1674</td>
<td>1221</td>
<td>Present work</td>
</tr>
<tr>
<td>(Na_2HPO_4\cdot 5 H_2O)</td>
<td>(PO_3^-)</td>
<td>1.9994</td>
<td>2.0011</td>
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<td>1514—1513</td>
<td>10</td>
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<tr>
<td>(MgHPO_4\cdot 6 H_2O)</td>
<td>(PO_3^-)</td>
<td>1.998</td>
<td>1.999</td>
<td>2210</td>
<td>1730</td>
<td>5</td>
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<tr>
<td>((NH_4)_2H_2P_2O_7)</td>
<td>(PO_3^-)</td>
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<td>2.0012</td>
<td>2420</td>
<td>1960—1940</td>
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<tr>
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<td>(PO_3^-)</td>
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<td>2.0012</td>
<td>2420</td>
<td>1960—1940</td>
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<tr>
<td>((NH_4)_2PO_3F\cdot H_2O)</td>
<td>(PO_3^-)</td>
<td>1.9994</td>
<td>2.0011</td>
<td>1822</td>
<td>1420—1409</td>
<td>13</td>
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<tr>
<td>(Na_2DPO_4\cdot 5 D_2O)</td>
<td>(PO_3^-)</td>
<td>1963</td>
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<td>2490</td>
<td>1847</td>
<td>14</td>
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<tr>
<td>(Mg(H_2PO_4)_2\cdot 6 H_2O)</td>
<td>(PO_3^-)</td>
<td>1.9977</td>
<td>2.0013</td>
<td>2490</td>
<td>1847</td>
<td>Present work</td>
</tr>
</tbody>
</table>

\(^3\) J. R. Morton, Chem. Rev. 64, 453 [1964].
\(^7\) R. E. Watson and A. J. Freeman, Phys. Rev. 123, 521 [1961].
\(^8\) C. A. Coulson, Volume Commémoratif Victor Henri, Contributions d l’Etude de la structure Moléculaire, 1948, p. 15.