EPR of Radiation Damage Centers in $NaNO_3$, $Sr(NO_3)_2$, BaS, and $MgC_2O_4 \cdot 2H_2O$

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$NaNO_3$, $Sr(NO_3)_2$, BaS, and $MgC_2O_4 \cdot 2H_2O$ powders have been gamma-irradiated at room temperature and their electron spin resonance spectra examined for paramagnetic species. The species identified were NO_3 and NO_2 radicals in the nitrates, SO_2^- and $\dot{S}$ in BaS, and $H_2C_2O_4^-$ in magnesium oxalate. Theoretical predictions agree with these assignments.

1. Introduction

It is well known that paramagnetic species can be trapped in a crystal matrix either by doping processes or by radiation damage of the host crystal, and that the resultant species can be studied by electron spin resonance (EPR) technique.

As a part of our project we have studied a large number of organic and inorganic chemicals, either in powder or single crystal form at room temperature. Although single crystal studies are more precise, we have investigated some materials in powder form because of growing difficulties. The present article describes such studies in the hope of identifying the species produced by gamma irradiation.

2. Experimental Considerations and Results

The powders were irradiated at room temperature with a cobalt-60 gamma-ray source (250 mc) for 24 hours. The EPR-experiments have been carried out at room temperature at the Hacettepe University with an X-band Varian-E-line commercial spectrometer with a 15″ magnet, using 5 mW microwave power. The radicals formed in $NaNO_3$, $Sr(NO_3)_2$, $MgC_2O_4 \cdot 2H_2O$ and BaS are found to be stable. The samples yield the same spectra after a few weeks, whilst before irradiation no spectra were observed. Irradiated $NaNO_3$ gave a main line of 10 gauss width with two very small bumps on each side. $Sr(NO_3)_2$ gave two overlapping lines and two bumps one each side of the two main lines.

BaS gave a strong line of 10 gauss width and a seven times weaker line of 2 gauss width at the high field side.

$MgC_2O_4 \cdot 2H_2O$ yields a strong line which is composed of two lines of equal intensity.

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3. Identification of Paramagnetic Species

Since the line width was 10 gauss and the spectroscopic splitting factor, g, was 2.0114, which is in good agreement with the results for $CO(NH_2)_2HNO_3$ [1] and lead nitrate [2], we come to the conclusion that in $NaNO_3$ the main radical species was the NO_3 radical. The assignment is partly based on the fact that the NO_3 species does not give hyperfine interaction with the N nucleus. This can be understood by considering the molecular orbitals of the system.

For an AB_3 molecule, in the case of a planar configuration (D_{3h} symmetry) the possible molecular orbitals between atomic 2p and 2s orbitals are listed in Table 1. Table 1 is based on the assumptions shown in Figure 1. Since the NO_3 molecule has less than 25 valence electrons it has a planar configuration [3] and its molecular orbitals

Table 1. The possible molecular orbitals for NO_3.

Symmetry and representation	Components of molecular orbitals		
	Nitrogen orbitals	Oxygen orbitals	Molecular orbitals
D_{3h}			
A_1'	s	$\frac{1}{\sqrt{3}}(s_1+s_2+s_3)$ $\frac{1}{\sqrt{3}}(p_{x1}+p_{x2}+p_{x3})$	$1\,a_1'$, $2\,a_1'$, $3\,a_1'$
A_2''	p_z	$\frac{1}{\sqrt{3}}(p_{z1}+p_{z2}+p_{z3})$	$1\,a_2''$, $2\,a_2''$
A_2'	none	$\frac{1}{\sqrt{3}}(p_{y1}+p_{y2}+p_{y3})$	$1\,a_2'$
A_1''	none	none	
E'	p_x, p_y	$\frac{1}{\sqrt{6}}(2\,s_1-s_2-s_3)$, $\frac{1}{\sqrt{2}}(s_2-s_3)$ $\frac{1}{\sqrt{6}}(2\,p_{x1}-p_{x2}-p_{x3})$, $\frac{1}{\sqrt{2}}(p_{x2}-p_{x3})$ $\frac{1}{\sqrt{6}}(2\,p_{y1}-p_{y2}-p_{y3})$, $\frac{1}{\sqrt{2}}(p_{y2}-p_{y3})$	$1\,e'$, $2\,e'$, $3\,e'$, $4\,e'$
E''	none	$\frac{1}{\sqrt{6}}(2\,p_{z1}-p_{z2}-p_{z3})$, $\frac{1}{\sqrt{2}}(p_{z2}-p_{z3})$	$1\,e''$

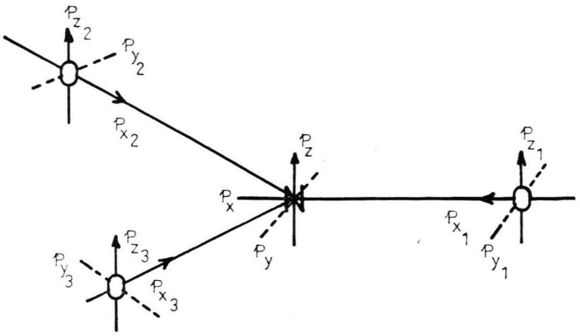

Fig. 1. The 2p atomic nitrogen and oxygen orbitals for NO_3. The arrowhead represents the positive lobe of the atomic orbitals.

have the following order of increasing energy:

$$(s_1\, s_2\, s_3)\,(1\,a_1')\,(1\,e')\,(1\,a_2'')\,(1\,e'')\,(2\,e')\,(1\,a_2')\,(2\,a_2'')\,(3\,e')\,(2\,a_1')$$

where oxygen lone-pair atomic orbitals are designated as s_1, s_2 and s_3. Therefore it is obvious that when the electron is in the $1\,a_2'$ orbital, the nitrogen hyperfine interaction is zero.

In $Sr(NO_3)_2$ the two main signals correspond to g values of 2.0155 and 2.0077. According to Walsh[3] these belong to the paramagnetic species NO_3 and NO_2 respectively.

In BaS we had expected to obtain the sulfur radical, as has been suggested for sodium thiosulfate[4]. During irradiation, however, BaS oxidized and therefore a line of 11.5 gauss width and a g value of 2.0144 was obtained. This is in good agreement with the results for sodium dithionite[5], and we therefore identify the species as SO_2^-. The signal appearing at the high field side of the main line with a g value of 1.9750 may be attributed to the sulfur radical[6].

There remains the discussion of the results obtained with magnesium oxalate. It would be worth while to carry out these measurements with single crystals, but unfortunately we were unable to crystallize the material. Magnesium oxalate should be hydrogen bonded as the other oxalates and we suggest the bonding shown in Figure 2. We propose that irradiation causes chemical rearrangements resulting in the radical species shown in Figure 3. This is in agreement with the two line spectrum. The simple spin Hamiltonian which describes the system is

$$\mathcal{K} = \beta\, \boldsymbol{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \boldsymbol{I}$$

where **S** and ***I*** are the electron and the proton spins respectively and **A** is the hyperfine coupling tensor in between. **A** cannot be measured accurately in a powder. The measured average value of the spectroscopic splitting factor, g, is 2.0104. This species has been proposed also on account of the results in urea oxalate[7].

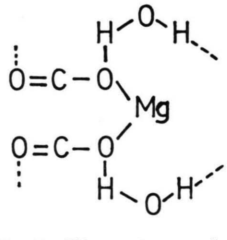

Fig. 2. Magnesium oxalate.

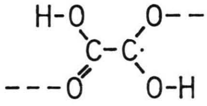

Fig. 3. The radical responsible for the EPR spectrum in irradiated magnesium oxalate.

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