ESR of $^{\cdot}NH_2$ and $^{\cdot}N_2H_4^+$ Free Radicals Produced by Gamma Irradiation in NH_3OHCl, $(NH_3OH)_2SO_4$ and $N_2H_6SO_4$

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Free radicals produced by gamma irradiation in single crystals of hydroxylammonium chloride, hydroxylammonium sulfate and hydrazinium sulfate have been investigated at room temperature with ESR. The radicals in the hydroxylammonium salts were identified as $^{\cdot}NH_2$ and that in hydrazinium sulfate as $^{\cdot}N_2H_4^+$. The ESR spectra of the radicals were unchanged and undiminished at room temperature more than eight months after irradiation. The g and hyperfine constants were found to be almost isotropic with an average $g = 2.0047$, $a_H = 2.0$ mT and $\alpha_N = 0.70$ mT for $^{\cdot}NH_2$ and $g = 2.0034$, $a_H = 1.10$ mT and $a_N = 1.15$ mT for $^{\cdot}N_2N_4^+$.

1. Introduction

Electron spin resonance (ESR) technique has been widely used in identifying the damage centers produced by high energy radiation [1–6]. Investigations on the g tensor and the hyperfine coupling constants of the spin carrying nuclei of the species give valuable information about the structure of the centers. Although a large number of organic and inorganic species have been produced and investigated, the studies on $^{\cdot}NH_2$ radical carry doubts [7–8] as the spectra cannot firmly be attributed to $^{\cdot}NH_2$. The isotropic hyperfine coupling constants for ^{14}N and ^{1}H have been analysed theoretically [9] for $^{\cdot}NH_2$ and $^{\cdot}N_2H_4^+$ but no experimental result could be given for $^{\cdot}NH_2$. We undertook this study on NH_3OHCl, $(NH_3OH)_2SO_4$ and $N_2H_6SO_4$ in the hope of obtaining the $^{\cdot}NH_2$ radical.

2. Experimental Details

The single crystals studied in this work were grown by slow evaporation of concentrated aqueous solutions. The hydroxylammonium chloride crystals are monocilinic. The hydroxylammonium sulfate crystals belong to the monoclinic $P2_1/c$ space group [10] and the unit cell dimensions are $a = 79.52$, $b = 73.35$, $c = 104.26$ nm and $\beta = 107°$. The unit cell contains four molecules. The hydrazinium sulfate crystal belongs to the orthorhombic $P2_12_12_1$ space group [11] with four formula units in its unit cell of dimensions $a = 82.51$, $b = 91.59$ and $c = 55.32$ nm. The crystallographic two-fold b axes of hydroxylammonium chloride and sulfate are shown in Figure 1. Suitably sized crystals have been irradiated with a ^{60}Co gamma source for 3 to 24 hours at room temperature, and the spectra have been recorded with a Varian x-band E 109 C model ESR spectrometer. The spectra were taken at intervals of 10° by rotating the crystals about three perpendicular axes. The g values were obtained by comparison of the centers of gravities of the spectra with a DPPH sample $g = 2.0036$.

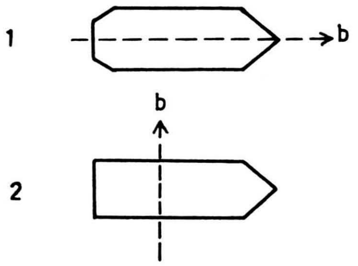

Fig. 1. The directions of the two-fold axes of NH_3OHCl and $(NH_3OH)_2SO_4$ single crystals.

3. Description of ESR Spectra

The ESR spectra of hydroxylammonium chloride and sulfate are clearest, as in Fig. 2, when the field is along or perpendicular to the crystallo-

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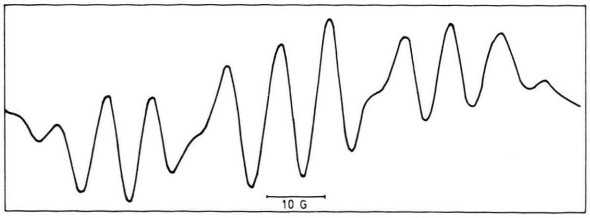

Fig. 2. ESR spectrum of gamma irradiated NH_3OHCl single crystal, H_0 is along the b axis.

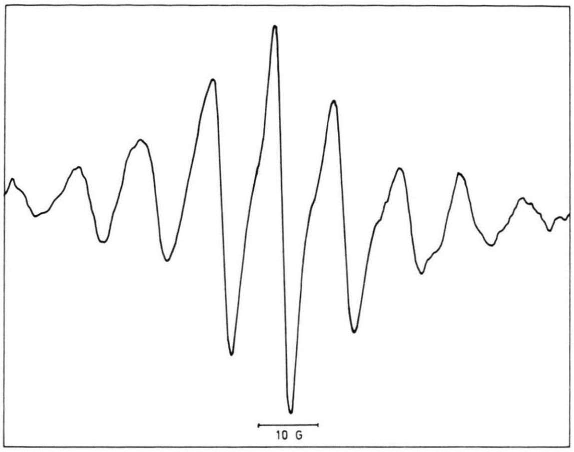

Fig. 3. ESR spectrum of gamma irradiated $N_2H_6SO_4$ single crystal, H_0 is along the crystallographic a axis and $T = 473$ K.

graphic two-fold axes of the crystal. This spectrum consists of 9 lines. It was impossible to follow the ESR lines of the magnetically nonequivalent molecules in the unit cells of the crystals. The ESR lines become somewhat sharper when the temperature is increased to a few degrees below the melting point.

The ESR spectrum of hydrazinium sulfate is simplest, as in Fig. 3, when the H_0 field is along the crystallographic axes and it becomes somewhat sharper when the temperature is increased up to 473 K. The results were perfectly reproducible during the study of eight months.

4. Discussion

The ESR spectra of hydroxylammonium chloride and sulfate consist of three triplets of intensity 1:2:1 when the H_0 field is along the crystallographic two-fold axes. These are the evidences of the hyperfine interaction of an electron with two protons and with a ^{14}N nucleus. The spectra can be interpreted in terms of the spin Hamiltonian

$$\mathscr{H} = \beta S g H_0 + S \sum_i a_H^i I_H^i + S a_N I_N , \qquad (1)$$

where β is the Bohr magneton and H_0 is the applied magnetic field. The first term represents the interaction of the electron spin, S, with the magnetic field H_0. The second and the third terms represent the hyperfine interaction of the electron spin with the ^1H ($I_H = \frac{1}{2}$) and ^{14}N ($I_N = 1$) nuclear spins, respectively. The synthesis of the spectrum of $^{\cdot}NH_2$ according to this Hamiltonian is shown in Fig. 4 and it is in agreement with the experimental spectrum in Figure 2. Thus we can firmly state that the paramagnetic center produced by gamma irradiation in NH_3OHCl and $(NH_3OH)_2SO_4$ is the $^{\cdot}NH_2$ radical. The g value and the hyperfine constants, a_H and a_N, were found to be almost isotropic for $^{\cdot}NH_2$ in NH_3OHCl and $(NH_3OH)_2SO_4$, and their values are given in Table 1.

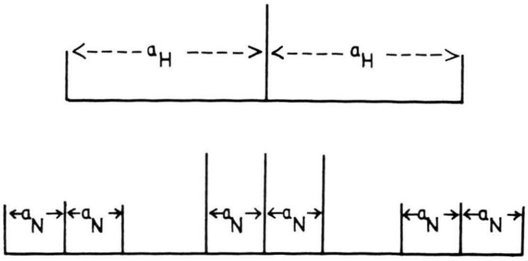

Fig. 4. Synthesis of the spectrum of $^{\cdot}NH_2$ radical; $a_H = 2.0$ and $a_N = 0.7$ mT.

Since the hyperfine coupling constants are almost isotropic it seems reasonable to conclude that $^{\cdot}NH_2$ is undergoing a rotational motion at room temperature which almost averages out the anisotropy of the hyperfine interaction, similarly to the NH_3^+ radical [12–13] in NH_4ClO_4. This can also be concluded if we consider the spin-lattice relaxation studies of protons [14–15] in NH_3OHCl and $(NH_3OH)_2SO_4$. In these studies the reorientational frequencies of the NH_3 groups at room temperature

Table 1. ESR results for $^{\cdot}NH_2$ and $^{\cdot}N_2H_4^+$.

Host crystal	Radical	g	a_H (mT)	a_N (mT)
NH_3OHCl $(NH_3OH)_2SO_4$	$^{\cdot}NH_2$	2.0047	2.0	0.70
$N_2H_6SO_4$	$^{\cdot}N_2H_4^+$	2.0034	1.1	1.15

were found to be 3.25×10^{10} and $3.33 \times 10^9\ s^{-1}$, respectively, for NH_3OHCl and $(NH_3OH)_2SO_4$. If we assume the presence of the same motions, these reorientation frequencies are well above the hyperfine constants as can be seen by converting the quantities in Table 1 into frequency units. When we compare our results for $^{\bullet}NH_2$ with the results given by Foner et al. [7] we see that in their study the intensities of the hyperfine lines do not agree with the synthesis of the spectrum in Figure 4. The triplet due to the nitrogen seems to have a central line which is too intense, and the triplet due to the protons is too weak. But their g value 2.00481 is in agreement with ours and the hyperfine coupling constants $a_N = 1.03$, $a_H = 2.39$ mT are not too different from the values of this study. Another work on $^{\bullet}NH_2$ in glycine [8] reports a 1:2:1 intensity pattern due to the protons but no resolved splitting of nitrogen. The reported values of $g = 2.00$ and $a_N = 1.39$ mT differ too much from the values of this study but $a_H = 2.10$ mT is almost in agreement with our result. It turns out that different intensity patterns and different hyperfine coupling constants of nitrogen have been observed for $^{\bullet}NH_2$ in these studies. The discrepancies my be due to the different rotational motion rates of $^{\bullet}NH_2$ and different relaxation times of nitrogen or due to a somewhat different electronic wavefunction of $^{\bullet}NH_2$ in these substances. The calculated result [9] $a_N = 0.73$ mT is in agreement with our experimental result but $a_H = 1.53$ mT is smaller than the value of this study. Another theoretical work on $^{\bullet}NH_2$ reports [16] $a_N = 0.82$ mT and $a_H = 1.62$ mT; these are closer to our results rather than the others [7–8].

The spectrum observed for gamma irradiated $N_2H_6SO_4$, Fig. 3, can be attributed to $^{\bullet}N_2H_4^+$ radical. The spin Hamiltonian for this radical is similar to the one given by (1), and the synthesis of the spectrum using $a_H = 1.10$ mT and $a_N = 1.15$ mT exhibits 9 blocks of lines [17], in excellent agreement with the spectrum in Figure 3. Although the 25 lines of $^{\bullet}N_2H_4^+$ are not resolved due to the line broadening this agreement is satisfactory. If we consider the proton spin-lattice relaxation study [18] on $N_2H_6SO_4$ we see that the reorientational frequency of the parent $N_2H_6^{+2}$ ion about the N–N bond at 300 K is $3.9 \times 10^9\ s^{-1}$, and this is well above the hyperfine constants in Table 1. Thus the anisotropic components almost average out and the residual dipolar interactions between the unpaired electron and the nuclei contribute to the line broadening. As a result we can state that $^{\bullet}N_2H_4^+$ is planar also in a solid since the observed $a_N/a_H \sim 1.05$ and the previous [17] explanations can be made. The theoretical work on $^{\bullet}N_2H_4^+$ reports $a_N = 0.78$ mT and $a_H = 1.06$ mT. This value of a_H agrees with our experimental result but the value of a_N is smaller than our result in Table 1.

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