Electron Spin Resonance of a Sigma-type Radical formed by *X*-Irradiation of Malonamide

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RECENTLY Rexroad *et al.*,[1] reported that the electron spin resonance spectra of γ-irradiated malonamide crystals showed a complex structure of which the major part was due to the $\dot{C}H(CONH_2)_2$ radical. The remainder of the structure was attributed to an unidentified second radical and was not further studied.

We have now identified this second radical as $H_2N{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}\dot{N}H$ through the study of the electron spin resonance spectra of *X*-irradiated crystals and its deuterated analogues. The electron spin resonance signal of this second radical disappeared almost completely on annealing at 100°, while the intensity of the signal due to the major radical remained only slightly changed.

From the proton nuclear magnetic resonance spectra of the deuterated malonamide dissolved in D_2O, it was found that the protons on the central carbon, $-CH_2-$, were deuterated almost completely and only some of the protons on nitrogen were deuterated. The ratio of the concentration of the $-CO-\dot{C}D-CO-$ radical to that of the $-CO-\dot{C}H-CO-$ was determined from the ratio of the areas of the integrated electron spin resonance first derivative signals and found to be approximately 4 : 1.

In the undeuterated crystals, the second radical

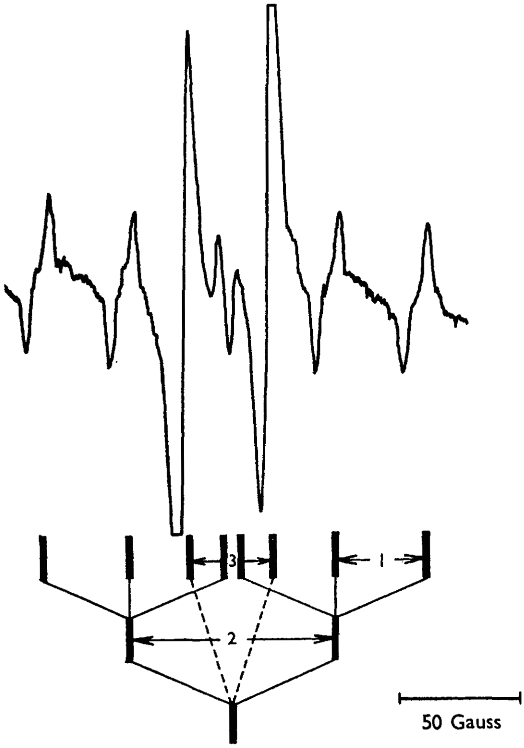

FIGURE 1. *Electron spin resonance spectrum of an undeuterated crystal of malonamide with* H‖a. 1. N-Splitting for $-CO\dot{N}H-$ 2. H-Splitting for $-CO\dot{N}H-$ 3. H-Splitting for $-\dot{C}H-$.

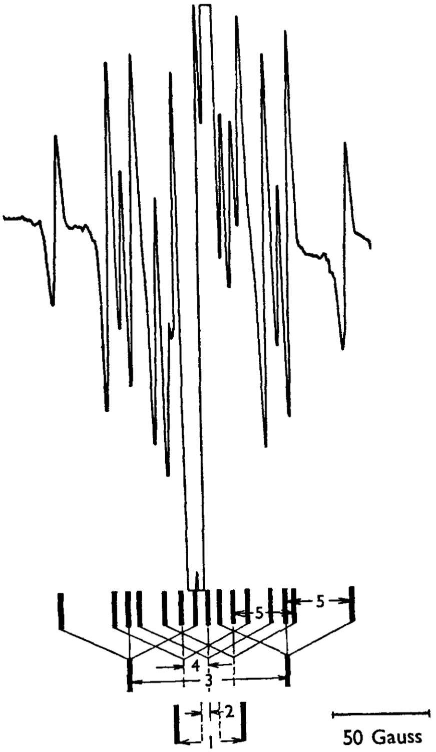

FIGURE 2. *Electron spin resonance spectrum of a deuterated crystal of malonamide with* H‖a. 1. H-Splitting for $-\dot{C}H-$. 2. D-Splitting for $-\dot{C}D-$. 3. H-Splitting for $-CO\dot{N}H$. 4. D-Splitting for $-CO\dot{N}D$. 5. N-Splitting.

showed hyperfine splittings due to the proton attached to the nitrogen, the nitrogen nucleus itself, and the protons of the central carbon atom. This last splitting would, *a priori*, be expected to be small, but can be seen clearly in the partially resolved outer lines in Figure 1. In the deuterated samples, hyperfine structure due to the radicals $-\mathrm{COCD_2{\cdot}CO\dot{N}D}-$ and $-\mathrm{COCD_2{\cdot}CONH}-$ can be seen. Splitting due to the deuterons on the central carbon atom, being much smaller than that for protons in the same position, was not observed.

The hyperfine splitting due to the nitrogen proton was found to be almost isotropic and approximately 80 gauss. That, due to the nitrogen nucleus, was found to be anisotropic and very nearly axially symmetric, approximately 35 gauss in the parallel direction and about 5 gauss in the perpendicular direction.

The complete determination of the hyperfine coupling tensors is being carried out now. Figures 1 and 2 show respectively the electron spin resonance spectrum of the undeuterated and deuterated crystal for an equivalent orientation.

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[1] H. N. Rexroad, Yu Hak Hahn, and W. J. Temple, *J. Chem. Phys.*, 1965, **42**, 324.