

Electron Spin Resonance Study of Some X-Irradiated Amide Single Crystals¹

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Abstract: Free radicals of the type $R_2\dot{C}CONH_2$ have been identified by their esr spectra in X-irradiated single crystals of propionamide, *n*-butyramide, and isobutyramide. Spectra were recorded and analyzed for a number of orientations of the crystals in the magnetic field. Principal values of the hyperfine coupling constants and their direction cosines with respect to the reference axes are given. The *g* values are nearly isotropic and the values measured along each of the reference axes are given. In certain orientations hyperfine splitting due to the ¹⁴N and ¹H nuclei of the amino group was resolved. An approximate ¹⁴N coupling tensor was derived for the radical in isobutyramide.

A number of amides have been shown to give identifiable free radicals in the frozen state or in powders when the sample is exposed to ionizing radiation.² More recently, solution spectra of free radicals derived from formamide and acetamide have been observed by using the hydroxyl radical generated in acid solution (H_2O_2 -Ti(III) system) for hydrogen atom abstraction.³ We report here the results of our study of X-irradiated single crystals of propionamide, *n*-butyramide, and isobutyramide.

Experimental Section

Single Crystals. Crystals of propionamide were grown from the melt or from the vapor at 85°. Crystals in which deuterium replaced hydrogen of the amino group were grown in the same way after several recrystallizations from deuterium oxide. The progress of the exchange was followed by infrared analysis (KBr disks). The *n*-butyramide and isobutyramide single crystals were obtained by slow evaporation of saturated ethanol solutions. The deuterium-exchanged crystals of these amides were grown from methanol-*d* solutions in a desiccator over $CaCl_2$ under a nitrogen atmosphere. The amino group protons were replaced by deuterium by repeated crystallization from deuterium oxide.

X-Ray Diffraction Results. The crystal structure of isobutyramide has not been previously determined. Precession and Weissenberg photographs show this amide to be monoclinic with unit cell parameters, $a = 9.69 \pm 0.02 \text{ \AA}$, $b = 5.97 \pm 0.01 \text{ \AA}$, $c = 10.11 \pm 0.02 \text{ \AA}$, and $\beta = 107.1^\circ$. Systematic absences were k odd for $(0k0)$ and h odd for $(h0l)$ indicating that the space group is $P2_1/a$. The observed density (1.013 g/cc) agrees well with the calculated value of 1.017 g/cc for four molecules per unit cell. Propionamide and *n*-butyramide are also monoclinic and the space group is $P2_1/a$. Turner and Lingafelter⁴ included these two amides in their study of a series of straight-chain unsubstituted amides.

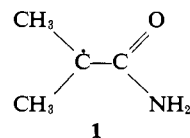
X-Irradiation of the Crystals. The crystals were irradiated using an X-ray unit operating at 50 kV and 20 mA. An exposure of 12 hr was used for a dose of $\sim 10^6$ rads. The isobutyramide could be irradiated and examined at room temperature. Propionamide and *n*-butyramide were irradiated and observed at lower temperatures ($\sim -78^\circ$) due to rapid radical loss at higher temperatures.

Esr Measurements. ESR spectra were recorded using a Varian V-4502 spectrometer with 100-kHz modulation. Isobutyramide crystals were aligned on a Teflon holder and inserted in a rotating cylindrical cavity. The orientation of the field with respect to the crystal was varied by rotating the magnet. The propionamide and *n*-butyramide crystals were mounted on a Teflon holder and observed using the Varian multipurpose cavity. The crystals were

cooled by a stream of nitrogen during the measurements. The angular dependence was studied by rotating the crystals with respect to the field. When not in use the crystals were stored in sealed vials under liquid nitrogen without serious loss of radicals. The mutually perpendicular reference axes are the crystallographic *a* and *b* and a third axis *c'*.

Results

Isobutyramide. In all orientations X-irradiated crystals of isobutyramide gave esr spectra consisting of a basic seven-line pattern with intensity ratios of 1:6:15:20:15:6:1. This indicates a radical with a group of six hydrogens coupling equally to the electron. Structure 1 is assigned to the radical in agreement with that suggested for the radical trapped in electron-



irradiated polycrystalline isobutyramide at room temperature.² The spectra were interpreted in terms of the spin Hamiltonian

$$\mathcal{H} = \beta H \cdot g \cdot S + \sum_i I_i \cdot A \cdot S$$

where β is the Bohr magneton, H is the magnetic field intensity, g is the spectroscopic splitting tensor, S is the electron spin operator, I_i is the nuclear spin operator of the i th nucleus, and A is a tensor representing the average coupling of the six methyl hydrogens. Since the methyl groups are rapidly rotating at room temperature, each of the hydrogens of a methyl group will have the same average coupling. The resolution was not sufficient to distinguish between the average coupling in the two methyl groups. The *g* values measured along the *a*, *b*, and *c'* axes were nearly isotropic, having a mean value of 2.0032 and a variation of -0.0004 to 0.0003.

From the measured splittings at various orientations of the crystal with respect to the magnetic field, the A^2 tensor was deduced. Principal values and direction cosines for the A tensor are given in Table I.

In some orientations additional hyperfine structure was resolved and attributed to coupling of the ¹⁴N and ¹H nuclei of the amino group. Figure 1a shows

(1) Supported in part by the Atomic Energy Commission.

(2) See M. T. Rogers, S. Bolte, and P. S. Rao, *J. Amer. Chem. Soc.*, **87**, 1875 (1965), and references cited there.

(3) P. Smith and P. B. Wood, *Can. J. Chem.*, **44**, 3085 (1966).

(4) J. D. Turner and E. C. Lingafelter, *Acta Cryst.*, **8**, 549 (1955).

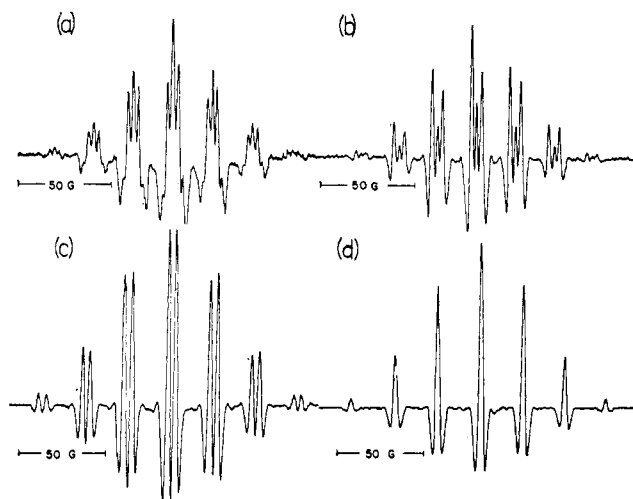


Figure 1. Second derivative esr spectra of radical 1 in isobutyramide: (a) spectrum observed when H is oriented along the c' axis; (b) similar to spectrum 1a, but deuterium replaced hydrogen on the amino group; (c) spectrum observed when H is oriented along the a axis; (d) similar to spectrum 1c, but deuterium replaced hydrogen in the amino group.

the basic seven-line pattern split into quintets with intensity ratios of 1:3:4:3:1. Equal coupling of the nitrogen and two hydrogens of the amino group would show such a pattern. In the same orientation, a crystal in which deuterium replaced the amino group hydrogens gave a group of seven triplets (Figure 1b) in agreement with this assignment. The triplet structure is due to ^{14}N coupling since the deuterium splitting is not large enough to be resolved. Deuterium splitting is only

Table I. Principal Values and Direction Cosines with Respect to the a , b , and c' Axes for Methyl Hydrogen Coupling in $(\text{CH}_3)_2\dot{\text{C}}\text{CONH}_2$

Principal values of A, G	Direction cosines		
	a	b	c'
+22.71	0.975	∓ 0.101	0.193
+21.64	0.117	± 0.991	-0.071
+20.76	-0.184	± 0.092	0.979

0.15 that of hydrogen in an equivalent position. A tensor for the ^{14}N coupling could be deduced from the spectra of the deuterium-labeled crystal. The principal values and direction cosines with respect to the a , b , and c' reference system derived by diagonalization of this tensor are given in Table II. These values are

Table II. Principal Values and Direction Cosines in the a , b , and c' Axis System for ^{14}N Coupling in $(\text{CH}_3)_2\dot{\text{C}}\text{CONH}_2$

Principal values of A_N , G	Direction cosines		
	a	b	c'
+0.23	0.7	∓ 0.7	-0.07
+0.40	0.7	± 0.7	0.0
+3.18	0.05	∓ 0.05	0.99

considered only approximate in view of the small magnitude of the splitting and the accompanying uncertainties in the measurements.

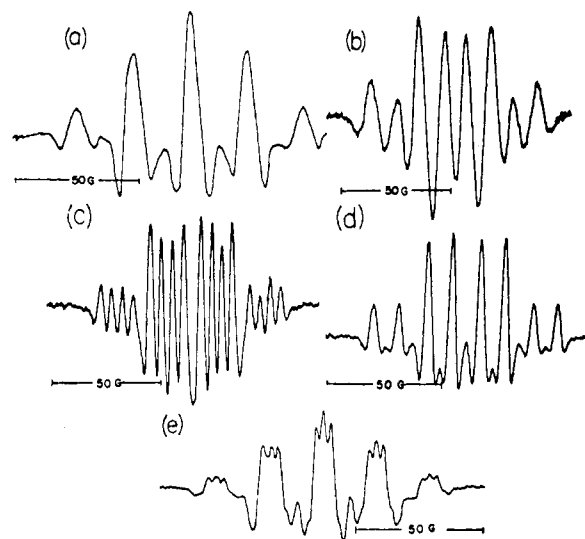
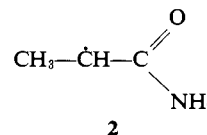


Figure 2. Second derivative esr spectra of radical 2 in propionamide: (a) spectrum observed when H is along the c' axis; (b) spectrum observed when H is in the bc' plane 15° from the b axis; (c) doublet pattern observed when H is in the ab plane 10° from the a axis; (d) similar to spectrum 2c but deuterium replaced the amino group hydrogens; (e) ^{14}N splitting observed when H is parallel to the c' axis.

When the magnetic field is aligned along the [100] direction, a group of seven doublets appears with a 4.2-G separation (Figure 1c). The doublet structure is due to one of the amino group hydrogens, since the corresponding orientation of the deuterium-labeled crystal gave a seven-line spectrum of binomial intensity ratios (Figure 1d). Again the deuterium splitting was below the resolution limit.

Propionamide Spectra. Spectra obtained for irradiated propionamide showed considerably more anisotropic character than did isobutyramide. In some orientations a five-line pattern is observed with relative intensity ratios of 1:4:6:4:1 (Figure 2a). For other orientations the five-line pattern splits into a pair of 1:3:3:1 quartets (Figure 2b). This behavior is attributed to the free radical resulting from the loss of an α -hydrogen atom from propionamide (2). The quar-



ter structure results from the averaged coupling of the methyl group hydrogens with the electron. The quartet splitting is nearly isotropic varying between 21 and 25 G. This coupling was not analyzed in detail.

The double quartet structure observed in the spectra is due to coupling with the remaining α -hydrogen. The separation between centers of the hyperfine quartets when the magnetic field explores the ab , ac' , and bc' planes is shown in Figure 3. The principal values and direction cosines for this α -hydrogen coupling are given in Table III.

In certain orientations additional hyperfine interactions are resolved. Figure 2c shows a doublet structure on the eight-line pattern. Deuterium substitution of the amino group hydrogens gave the eight-line pattern shown in Figure 2d for this orientation indicating

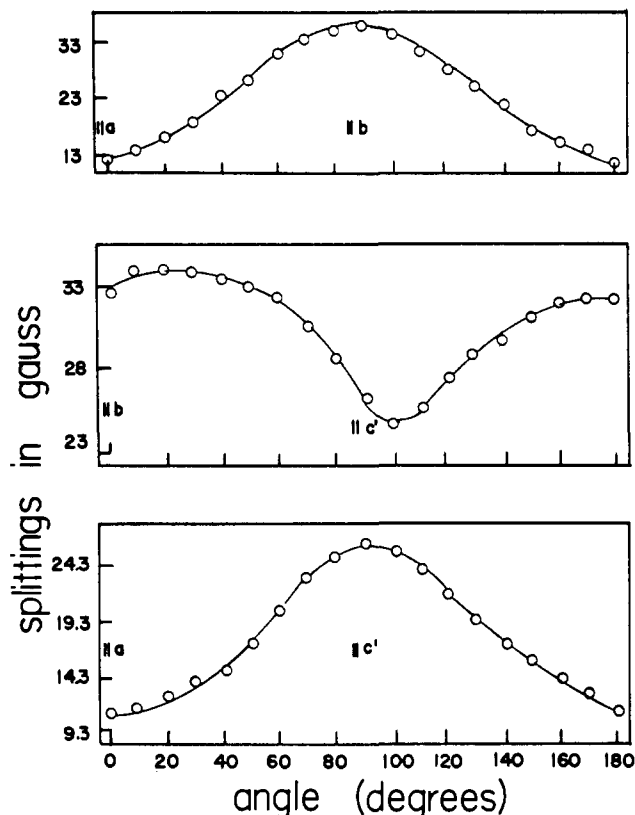


Figure 3. Variation of the α -hydrogen coupling in the ab , ac' , and bc' planes.

that this interaction is due to a single amino group hydrogen. From the 4.88-G doublet splitting measured from the spectrum of the hydrogen-containing specimen, a splitting of 0.73 G is predicted for a deuterium atom in the same position. This splitting is smaller than the line width observed in the spectrum of the deuterium-labeled crystal and removes the possibility that the splitting observed in the hydrogen spectrum is due to poorly resolved nitrogen splitting. A hyperfine interaction due to the nitrogen nucleus can also be resolved in some orientations (Figure 2e). However, this splitting could not be resolved in a sufficient number of orientations to obtain even an approximate nitrogen coupling tensor.

Table III. Principal Values and Direction Cosines for the α -Hydrogen Coupling in the abc' System in $\text{CH}_3\dot{\text{C}}\text{HCONH}_2$

Principal values of A_{H} , G	Direction cosines		
	a	b	c'
-10.61	0.990	± 0.093	0.110
-34.09	0.115	∓ 0.97	0.214
-24.29	0.087	± 0.224	0.971

***n*-Butyramide Spectra.** Figure 4a shows the esr spectrum of an irradiated crystal of *n*-butyramide when the field is directed parallel to the c' axis. It consists of two triplets with intensity ratios of 1:2:1. In the ab plane at 120° from b a seven-line pattern is seen with intensity ratios of 1:1:1:2:1:1:1 (Figure 4b). More complex spectra are observed in the bc'

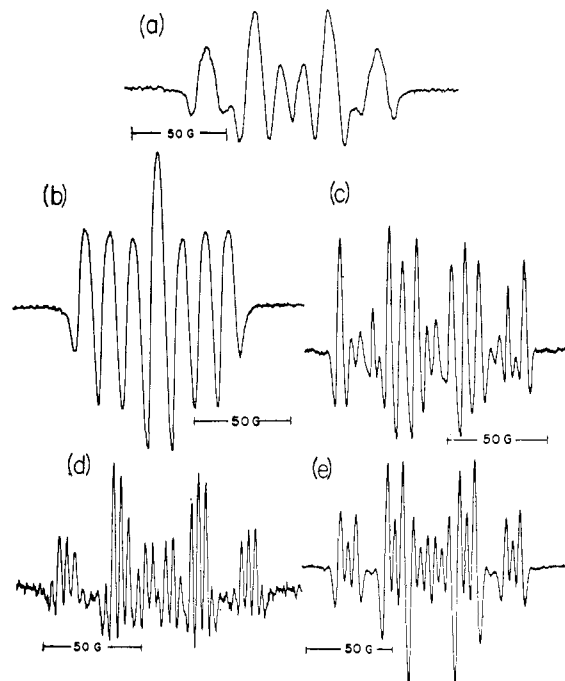
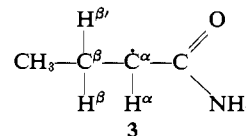


Figure 4. Second derivative esr spectra of radical 3 in *n*-butyramide: (a) spectrum observed when H is parallel to the c' axis; (b) spectrum observed in the ab plane when H is 120° from b ; (c) spectrum observed in the bc' plane when H is 30° from c' ; (d) similar to spectrum 4a with higher resolution; (e) similar to spectrum 4d but deuterium replaced the amino group hydrogens.

plane. An example is shown in Figure 4c. The observed spectra are attributed to the radical shown (3).



In this radical the β -hydrogens are not magnetically equivalent due to restricted motion about the $\text{C}^{\beta}-\text{C}^{\alpha}$ bond. The coupling constant for one of the β -hydrogens, A_{β} , is considerably larger than the other, $A_{\beta'}$. The coupling in each case is nearly isotropic ($A_{\beta} = 36.5 \pm 2$ G and $A_{\beta'} = 23.5 \pm 2$ G in the ab plane). The coupling constant of the third hydrogen exhibits a large variation with orientation typical of α -hydrogens. The principal values and direction cosines with respect to the a , b , and c' axes for the α -hydrogen are given in Table IV.

Table IV. Principal Values and Direction Cosines in the abc' Axis System for the α -Hydrogen Coupling in $\text{CH}_3\dot{\text{C}}\text{H}_2\text{C}^{\alpha}\text{HCONH}_2$

Principal values of A_{H} , G	Direction cosines		
	a	b	c'
-9.40	0.970	∓ 0.231	-0.082
-35.00	0.238	± 0.966	0.098
-24.60	0.056	∓ 0.115	0.992

When the sweep modulation was reduced the orientation in which the broad line spectrum shown in Figure 4a was observed gave the spectrum shown in Figure 4d. This additional hyperfine structure with approximate intensity ratios of 1:3:4:3:1 is attributed to equal

coupling of the nitrogen and the two hydrogens of the amino group. When the amino group hydrogens are replaced by deuterium, the same orientation gives the spectrum shown in Figure 4e. The splitting due to the amino group hydrogens is now absent from the spectrum and a group of six triplets is observed. The deuterium splitting is too small to be resolved.

g Factors. The *g* factors were measured for each of the radicals using a trace of solid DPPH as a reference. Values calculated for the *g* factors when the field was oriented along each of the reference axes are listed in Table V.

Table V. *g* Factors Measured along the *a*, *b*, and *c'* Axes

Radical	<i>g</i> factors obsd		
	<i>a</i>	<i>b</i>	<i>c'</i>
CH ₃ ĊCONH ₂	2.0028	2.0037	2.0024
CH ₃ CH ₂ ĊCONH ₂	2.0034	2.0037	2.0029
(CH ₃) ₂ ĊCONH ₂	2.0033	2.0035	2.0028

Discussion

Each of the amides studied give esr spectra that are consistent with the general formula R₂ĊCONH₂ for the radicals. They are considered planar, π-type radicals in which the odd electron is largely localized in a p orbital centered on the trigonal (sp² hybridized) α-carbon atom. The radicals in propionamide and *n*-butyramide possess an α-hydrogen as indicated by the pronounced anisotropy in the hyperfine splitting pattern. The magnitude of the isotropic coupling constants derived from the principal values of the A_H tensors (Tables III and IV) is 23 G for the radicals in both propionamide and *n*-butyramide. This value agrees well with the 23-G coupling observed in irradiated amorphous acetamide,⁵ but somewhat lower than the 24.7-G splitting observed in electron-irradiated amorphous propionamide.² Many radicals of the type -ĊHCO- give isotropic α-hydrogen coupling constants in the range 20–24 G.

The β-hydrogen coupling constants for the radical in isobutyramide were evaluated even though the variation of the splitting was small compared with α-hydrogen coupling. The methyl groups of this radical are undergoing rapid reorientations compared to the microwave frequency (~9.3 GHz) used for observation. This was the case even at 77°K (boiling nitrogen temperature) since spectra recorded at this temperature show no measurable differences in the hyperfine coupling. The principal values given in Table I for the hyperfine interaction tensor were used to calculate the isotropic contribution to the hyperfine coupling. Our value of +21.7 G is in excellent agreement with that observed by Smith,⁶ who found 21.4 G for this interaction in solution using a flow method.

Box and Freund⁷ have pointed out that the maximum value for the hyperfine splitting in a π radical of similar type derived from α-aminoisobutyric acid should be observed when the magnetic field is oriented in the radical plane, and perpendicular to the bond between

(5) C. F. Luck and W. Gordy, *J. Amer. Chem. Soc.*, **78**, 3240 (1956).

(6) Unpublished observations by P. Smith and M. Fox using the flow method described in ref 3. We appreciate Dr. Smith's permission to quote these results prior to their publication.

(7) H. C. Box and H. G. Freund, *J. Chem. Phys.*, **44**, 2345 (1966).

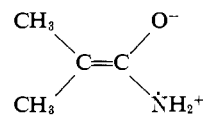
the α-carbon atom and the carboxamide carbon. The minimum value should appear when the field is directed along the symmetry axis of the p orbital containing the π electron. McConnell and Robertson⁸ have concluded that the minimum *g* factor in π-type radicals should also be observed when the field is directed along the symmetry axis of the π-electron orbital. We have measured the *g* factors for the radicals in the amides studied when the field was directed along each of the *a*, *b*, and *c'* axes. Reference to Tables I and V shows that the direction cosines for the minimum principal value of the β-hydrogen coupling constants lies in the approximate direction of the minimum *g* factor.

Restricted motion of the methylene group hydrogens of the radical in *n*-butyramide renders these hydrogens magnetically distinguishable. When the magnetic field explores the *ab* plane, one of these hydrogens shows a coupling constant of 36.5 G and the other a coupling of 23.5 G which remain nearly constant (±2 G). The empirical equation⁹

$$a_H(\theta) = B_0 + B \cos^2 \theta$$

was used to calculate the mean orientation of the methylene hydrogens with respect to the symmetry axis of the p (π) orbital. In this equation, *B*₀ and *B* are empirical constants and θ is the angle between the C(β)-H(β) bond and the symmetry axis of the p orbital, both projected on a plane perpendicular to the C(α)-C(β) bond. Since *B*₀ is certainly small, and may be zero, it is neglected in comparison with *B* which is taken as 42 G. The angle of twist for the β-hydrogen with the larger coupling constant is then 21° and that of the hydrogen with the 23.5-G splitting is 138°. The difference between these angles is 117° which is near the 120° angle expected for the projection of tetrahedrally bonded hydrogens on the plane.

The ¹⁴N hyperfine interaction observed for the radical in isobutyramide shows the expected cylindrical symmetry in the principal values of A_N recorded in Table II. This has been found to be the case for a number of nitrogen-centered π radicals.¹⁰ The large principal value has direction cosines (0.05, ∓0.05, 0.99) where the sign duality of the cosine with respect to the unique *b* axis results from site splitting in the monoclinic crystal. This direction corresponds to the direction parallel to the nitrogen p (π) orbital. A contribution to the resonance hybrid of the structure



could account for these observations. This requires that the atoms of the carboxamide group are coplanar with the trigonal α-carbon. Comparison of the direction cosines for the minimum A_H coupling constant, which should occur when the field is parallel to the p orbital of the α-carbon, and the direction of the maximum ¹⁴N coupling are approximately the same.

(8) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

(9) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(10) H. W. Shields, P. J. Hamrick and W. Redwine, *ibid.*, **46**, 2510 (1967); A. Horsfield, J. R. Morton, J. R. Rowlands, and D. H. Whiffin, *Mol. Phys.*, **5**, 241 (1962); J. R. Rowlands, *ibid.*, **5**, 565 (1962); J. R. Morton, *J. Phys. Chem. Solids*, **24**, 209 (1963).

Other features of the spectra for this radical agree with this interpretation. The quintet structure that appears when the field is oriented perpendicular to the radical plane suggests that the ^{14}N and the amino group hydrogens couple equally with the electron. When the magnetic field is directed along the a axis a group of well-resolved doublets appears in the hyperfine pattern. For this same orientation the doublet structure collapses to the basic seven-line pattern when deuterium replaces hydrogen on the amino group. The maximum doublet splitting attributed to an amino group hydrogen appears in the orientation very near the direction of the maximum value for the methyl group coupling. The maximum coupling of the methyl groups is predicted⁷ to occur when the field is in the radical plane and perpendicular to the $\text{C}(\alpha)\text{-CONH}_2$ bond. Theory predicts and observations confirm¹⁰ that the maximum

coupling for hydrogen bonded to nitrogen in a nitrogen-centered π radical occurs when the field is in the nodal plane of the nitrogen p orbital and perpendicular to the N-H bond. The minimum coupling for such hydrogen occurs when the field is parallel to the N-H bond. The qualitative features of the spectra associated with the amino group protons for each of the radicals studied agree with these predictions. It is possible that the doublet structure from the amino group proton arises from electron spin density on oxygen with coupling through the hydrogen bond network. This would require an unreasonably large spin density on oxygen to explain the magnitude of the splitting observed (3.1 G in the case of radical 1).

Acknowledgment. We wish to thank Dr. H. Wallace Baird for his assistance with the X-ray diffraction results.

The Crystal Structure of the Ethyl Grignard Reagent, Ethylmagnesium Bromide Dietherate¹

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Abstract: An X-ray diffraction study of the ethyl Grignard reagent in diethyl ether was undertaken to establish the structure of this reagent in the solid state. Crystals of $\text{C}_2\text{H}_5\text{MgBr}\cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ are monoclinic with space group $\text{P}2_1/c$ and four formula units per cell of dimensions $a = 13.18 \text{ \AA}$, $b = 10.27 \text{ \AA}$, $c = 11.42 \text{ \AA}$, and $\beta = 103.3^\circ$. The structure consists of the packing of discrete monomer units with a bromine atom, an ethyl group, and two ether groups tetrahedrally coordinated to a magnesium atom.

Investigations into the nature of the Grignard reagent have been numerous and diverse in the recent literature. This problem is discussed in two recent reviews^{3,4} which testify to the scope of the research done and the problems involved in its interpretation. The purpose of this paper is to present and discuss the details of the crystal structure refinement of the ethyl Grignard reagent. A preliminary account of this work was reported earlier.⁵

Experimental Section

The ethyl Grignard solution was prepared in the conventional way in diethyl ether in about 1 M concentration. The details of the solution preparation, purification, and transfer into glass capillaries will not be given here since they are similar to those reported by Stucky in his work⁶ on the phenyl Grignard reagent. Single crystals were grown in Lindemann glass capillaries by cooling with a

cold nitrogen gas stream. Crystals during growth were consistently prismatic with monoclinic C_{2h} point symmetry. No effort was made to determine the crystal melting point accurately, but it is estimated to be about 15° .

Ethylmagnesium bromide dietherate crystallizes in the monoclinic system with cell parameters of $a = 13.18 \pm 0.03$, $b = 10.27 \pm 0.03$, $c = 11.42 \pm 0.03 \text{ \AA}$, and $\beta = 103.3 \pm 0.3^\circ$. The calculated density on the basis of four formula units per cell is 1.24 g/cm^3 . It was not possible to obtain an experimental density. The systematic absences of $\{h0l\}$, $l = 2n + 1$, and $\{0k0\}$, $k = 2n + 1$, establish the space group as $\text{P}2_1/c$. All atoms in the cell are in the general positions⁷ $\pm(x, y, z; x, 1/2 - y, 1/2 + z)$.

The following nine zones of intensity data were measured on the precession camera on two crystals using Zr-filtered $\text{Mo K}\alpha$ radiation: $\{0kl\}$, $\{1kl\}$, and $\{2kl\}$ on the first crystal and $\{h0l\}$, $\{h1l\}$, $\{h2l\}$, $\{hk0\}$, $\{hk1\}$, and $\{hk2\}$ on the second crystal. The data were measured at about -75° . The entire camera was enclosed in a polyethylene tent as this proved to be the only effective way of preventing icing of the capillary. Crystals used were cylindrical in shape with diameter and length of about 0.3 mm.

Timed exposures were taken according to ar^n with $a = 1 \text{ min}$, $r = 2$, and $n = 0, 1, \dots, 8$. The intensities were measured by comparison with a series of standard intensities. On those photographs showing mm symmetry, two quadrants were judged and then averaged. A total of 979 observed reflections was judged.

The errors in the structure factors were assigned using a modified Hughes scheme⁸ so that

(7) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 99.

(8) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 328.

(1) Contribution No. 2271; work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) Central Research Department, E. I. du Pont de Nemours and Co., Wilmington, Del. (b) Deceased, Oct 9, 1963.

(3) B. J. Wakefield, *Organometal. Chem. Rev.*, **1**, 131 (1966).

(4) E. C. Ashby, *Quart. Rev.* (London), **21**, 259 (1967).

(5) L. J. Guggenberger and R. E. Rundle, *J. Am. Chem. Soc.*, **86**, 5344 (1964).

(6) G. Stucky and R. E. Rundle, *ibid.*, **86**, 4825 (1964); G. Stucky and R. E. Rundle, *ibid.*, **85**, 1002 (1963).