A STUDY OF THE FREE RADICALS IN IRRADIATED AMIDES BY ELECTRON SPIN RESONANCE SPECTROSCOPY

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ABSTRACT

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by Sara-Jo Kleinheksel Bolte

Polycrystalline amides representative of hydrocarbon substitution on both the nitrogen and the carbonyl carbon, and two related carboxylic acids have been irradiated with 1 Mev. electrons at liquid air temperature. The free radicals formed by irradiation were studied by electron spin resonance spectroscopy in the 9 Kmc. region at liquid air temperature, using a spectrometer built at Michigan State University and a Varian E.S.R. spectrometer. The hyperfine spectra observed were used to determine the number and type of nuclei interacting with the spin of the unpaired electron and their isotropic coupling constants. From this information the free radicals formed by irradiation were identified and a scheme for the prediction of the site of radiation damage in some compounds is suggested.

The spectra were analyzed by comparison with Gaussian derivative curves calculated by the MISTIC computer. These theoretical curves were computed for the interaction of the spin of the unpaired electron with probable numbers of equivalent protons, using various combinations of peak spacing and line width. Interaction with the odd electron spin was assumed to be limited to alpha- and beta-nuclei, and the structure of the free radical was assumed to be similar to that of the parent compound.

The radiation damage observed in the amides and acids occurred only within one of the alkyl groups of the molecule. An alkyl group bonded

to the nitrogen of an amide was always attacked in preference to a group attached to the carbonyl carbon. In most cases a hydrogen was removed, but in some cases a carbon-carbon bond was broken rather than a carbon-hydrogen bond. We have observed no other type of radiation damage. The carboxylic acids and the amides analogous to them form the same radical when irradiated.

The particular site of hydrogen removal within the alkyl group is found to be consistent with the following generalization: (1) a methyl carbon-hydrogen bond is broken only if no other carbon-hydrogen or carbon-carbon bond is present in the preferred alkyl group, (2) a proton is removed from a CH_2 group next to a methyl group in preference to a similar group adjacent to the nitrogen, (3) for a tertiary carbon the carbon-carbon bond to the carbonyl group is broken in preference to the carbon-carbon bond to a methyl group.

Radical formation can be accurately described by these generalizations for N-substituted amides, but some anomalies appear when the only alkyl group present is adjacent to carbonyl. The radical formed from n-butyramide cannot be identified with certainty, but carbon-carbon bond breakage and loss of the terminal methyl group is suggested. For isobutyramide significant amounts of two radicals appear to be present, with either a methyl group or a hydrogen atom being removed from the tertiary carbon adjacent to the carbonyl group. The radical formed by the loss of hydrogen is the more stable.

Substitution of two different types of alkyl groups on the nitrogen gives the only other example observed of the formation of significant amount of more than one radical. Branched alkyl groups give some extra spectral lines which could not be identified accurately, but which probably indicate the presence of small amounts of radicals other than the predominent species identified. The presence of two substituents of the same kind on nitrogen has no significant effect on the site of radiation damage or on the spectrum observed.

In all cases the coupling constant observed for an alkyl radical on the nitrogen is smaller than that for a similar alkyl radical bonded to the carbonyl. Thus N-methylamides give a value of 16.8 to 19.6 gauss, while the generally accepted coupling constant for acetamide is about 23 gauss. N-ethylamides give a coupling constant from 20.1 to 20.6, while that of propionamide is 24.7 gauss. This difference indicates that some of the unpaired electron spin is localized on the nitrogen atom, even though no interaction from this nucleus is observed.

We feel that these results will give significant assistance in the identification of radicals in future studies of irradiated organic molecules.

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INTRODUCTION

In recent years the effect of radiation on biological materials has become of great interest. The immediate result of irradiation is the breaking of chemical bonds and formation of free radicals. Electron spin resonance may be used to identify these radicals and to obtain information about their electronic structure. The radiation damage in biological materials is too complex to be directly analyzed, and the study of simpler compounds with related bonding may be taken as a beginning to the understanding of their results.

The irradiation of amides produces radicals which are stable for long periods of time at low temperatures, and which may serve as suitable models for radiation damage to amide linkages in proteins. In the work reported here a group of amides have been irradiated as polycrystalline solids at low temperatures, and the radicals formed are identified and discussed. In order to determine the factors dictating the stability of radicals, amides having a variety of substituents on both carbon and nitrogen were used.

Most previous work on irradiated simple organic compounds has been limited to those which are solid at room temperature. In the present study amides which are liquid at room temperature have been included.

HISTORICAL AND THEORETICAL BACKGROUND

Introduction

The absorption of energy from a high frequency magnetic field by a paramagnetic substance placed in a steady perpendicular magnetic field was first observed in Russia by Zavoisky[1] in 1945, using solutions of manganese salts. Using similar samples the American investigators Cummerow and Halliday[2], and Bagguley and Griffiths[3] in England shortly afterwards also observed electron spin resonance (E.S.R.), as this phenomenon came to be called. Studies of the paramagnetic salts of the transition elements and later those of the rare earths were undertaken by numerous investigators.

The study of naturally occurring organic free radicals by E.S.R. did not begin until 1949 when the first observation was made by Holden, Kittel, Merritt and Yager.[4] During the same year E.S.R. was first used in the study of radiation damage when Hutchison[5] investigated the color centers formed in LiF and KCl due to irradiation with neutrons. In 1951 Schneider, Day, and Stein[6] irradiated samples of polymethylmethacrylate, and made the first study of the E.S.R. spectra of free radicals formed by radiation damage. Surveys[7-12] of the experimental work in E.S.R., discussions[9-22] of the general theoretical aspects of E.S.R., and more specific articles on the theoretical considerations for organic free radicals[23-27] may be found in the literature.

General Theory

The electron has an internal angular momentum of $1/2(h/2\pi)$. This is more simply stated by saying that the electron has a spin of 1/2. As a result there is an inherent magnetic moment rigidly bound to the axis of spin. The presence of an external field then will align the electron in accordance with the restriction that for small particles the component of angular momentum along the field can take only certain values. For the case of an electron, the spin and the magnetic moment must be either parallel or antiparallel to the field. The electron then has two energy states, $-1/2\ g\beta H$, the ground state, and $1/2\ g\beta H$, the excited state. Transitions between such states, known as Zeeman levels, give rise to paramagnetic resonance. In order to induce a transition, the energy of a quantum of high frequency energy must equal the energy difference between the states.

$$h\nu = \Delta E = g\beta H \tag{1}$$

Here h is Planck's constant, and β is the Bohr magneton, equal to $eh/4\pi mc$, which converts angular momentum to magnetic moment in electromagnetic c.g.s. units. H, the magnetic field strength and ν, the frequency, are obviously dependent upon the experimental conditions chosen. g is known as the spectroscopic splitting factor, and is experimentally determined. The value of g is a characteristic of the particular absorption line, and measures the rate at which Zeeman levels diverge with an increase in the magnetic field.

For an atom or ion free from all other effects, this g factor would be expected to be the Landé g factor;[11]

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad (2)$$

where:

S is the spin angular momentum quantum number

L is the orbital angular momentum quantum number

J is the total angular momentum quantum number.

Dirac derived the value of 2 for g for a free spin. However, even in molecular beam experiments, where the spins may be considered as free the use of exactly 2 leads to serious errors. This is because the magnetic moment of the electron, due to relativistic effects, is not exactly equal to the Bohr magneton. The true free electron value which should be used is $g = 2.0023$. In practice, the local magnetic and electric fields existing within the substances studied cause the value of g to vary greatly from the free atom value.

Unlike nuclei, electrons are indistinguishable from one another and in a molecule they are not constrained to a particular area. As stated in the Pauli Principle, the total wave functions of electrons must be asymmetric with respect to the interchange of two electrons. Hence the net electron spin of the molecule under study should be used rather than the individual electron spins. For all spin paired molecules, this net spin is obviously zero, and no transitions can be observed.

Taking S as the total spin of a molecule the magnetic quantum number, M_s, can have values S, (S-1), ..., -S. That is, there are 2S+1 values, each of which has energy $M_s g\beta H$ in a field H. The selection rule for transitions between these states is $\Delta M_s = \pm 1$. In the absence of any other effects, all allowed transitions are degenerate.

The degeneracy of the 2S allowed transitions can be lifted through the Stark effect by the presence of electrostatic crystalline fields of the proper symmetry in the samples under study. The various transitions then occur at different values of the magnetic field, giving rise to fine structure in the spectrum. Free radicals such as are under consideration here have $S = 1/2$. Therefore, in spectra of these substances fine structure does not occur.

In a free ion, the motion of electrons in their orbits sets up a magnetic field which interacts with the spin moments. This interaction is known as spin-orbital coupling. An external magnetic field would orient both the spin and the orbit, and transitions would occur between energy levels determined by a combination of these moments. It is this effect which gives values of g greatly different from 2 in some systems. In the presence of internal fields, however, the orbits may be greatly distorted and the resultant orbital moment will have directional properties. In such cases the orbital moment can be greatly reduced, and it is not readily reoriented in the presence of an external field. In free radicals there is a high asymmetry of the internal field due to the strongly directed covalent bonds which are not easily redirected. This quenches the spin-orbital coupling and gives, for free radicals, a g value very close to that of the free spin case.

The spin moment of the electron is quantized along the resultant of the internal and external fields and anisotropy can result. For free radicals, in which spin-orbital coupling is quenched, such anisotropy is very small.

An atomic nucleus which has a spin and the associated magnetic moment, has orientations with respect to the field and the electron spin, so that the extra magnetic field due to the nuclear magnetic moment averaged over the electron orbit is not zero. This field adds to the external magnetic field and there is an interaction between the moment of the nucleus and the electronic magnetic moment. With a nuclear spin of I, 2I + 1 orientations are possible for the nucleus with respect to the external field. The applicable selection rule during electronic transitions is $\Delta m_1 = 0$, that is, the nucleus does not change orientation. Thus each electronic level is split into 2I + 1 components, giving allowed transitions at 2I + 1 different values of the external field. This hyperfine splitting is the main source of information in the spectra of free radicals. As long as the applied field is much stronger than the field produced by the nucleus, the spacings between adjacent hyperfine components are equal.

The energy of interaction is normally expressed in the form of a Hamiltonian. Abragam and Pryce[21] have worked out a spin Hamiltonian for the case of one nucleus contributing to the hyperfine structure. Spin-orbital coupling contributions to the energy are omitted in the equation presented here since the coupling is quenched in free radicals. Also omitted are any interactions between electronic spins. All radicals discussed are formed by radiation damage giving a very low concentration making interaction negligible.

$$\mathcal{H} = g_e g_N \beta \beta_N \left[\frac{\bar{S}_e \cdot I_N}{|\bar{r}_e - \bar{r}_N|^3} - \frac{3(\bar{S}_e \cdot \bar{r})(I_N \cdot \bar{r})}{|\bar{r}_e - \bar{r}_N|^5} - \frac{8\pi}{3} \bar{S}_e \cdot I_N \delta(\bar{r}_e - \bar{r}_N) \right] \quad (3)$$

where:

g_e = g-value of the electron

g_N = g-value of the nucleus

β = Bohr magneton

β_N = nuclear magneton
$\bar{S}_e$ = electron spin operator
$\bar{I}_N$ = nuclear spin operator
$\bar{r}_e$ = vector position of the electron
$\bar{r}_N$ = vector position of the nucleus
$\delta(\bar{r}_e-\bar{r}_N)$ = Dirac delta function for the distance between the electron and the nucleus normalized in 3 dimensions.

This Hamiltonian is composed of two parts. The first part;

$$g_e g_N \beta\beta_N \left[\frac{\bar{S}_e \cdot \bar{I}_N}{|\bar{r}_e-\bar{r}_N|^3} - \frac{3(\bar{S}_e \cdot \bar{r})(\bar{I}_N \cdot \bar{r})}{|\bar{r}_e-\bar{r}_N|^5} \right] \tag{3a}$$

varies with the angle between the nuclear moment and the direction of the external field, giving rise to anisotropy of the hyperfine interaction. This anisotropic part is very important in single crystals, but in non-crystalline systems the directional component is spread out over the whole solid angle. In liquids, due to the rapid, random molecular motion it goes to zero[28] and causes no loss of resolution.

The second part;

$$g_e g_N \beta\beta_N \left[-\frac{8\pi}{3} \bar{S}_e \cdot \bar{I}_N \, \delta(\bar{r}_e-\bar{r}_N) \right] \tag{3b}$$

is often called the Fermi contact term, and is non-directional, giving isotropic splitting.[29] The Dirac delta function in this term goes to zero for all orbitals which have a node at the nucleus. The unpaired electron spin must therefore have a finite probability of being at the nucleus in question to give a value for the isotropic term.

Line Widths

In general there are four parameters of interest in any E.S.R. spectrum: (1) the g value, (2) fine structure splitting values, (3) line width, and (4) hyperfine structure splitting values.

The first two parameters have little significance in free radicals, since the g value is always very close to 2 due to the quenching of spin orbital coupling, and fine structure does not occur unless more than one unpaired spin is present in the molecule. Since the free radicals considered here are neither biradicals nor in triplet states, such fine structure is not possible.

The two factors of interest in the radicals considered are then, line widths and hyperfine splitting values.

If the effect of the interaction of the odd electron spin with the fields of neighboring dipoles cannot be resolved into its separate fine or hyperfine components, a broadening of the spectral lines results, known as dipolar or spin-spin broadening. In non-crystalline samples, such an effect results from the anisotropic part of the interaction of the spin with magnetic nuclei. In liquid samples the rapid, random motion of the molecules is sufficient to average this effect out to zero, but for amorphous samples, the effect is merely spread out over the total solid angle and produces line broadening. This type of broadening gives a Gaussian shape to the line. In general, interaction between various unpaired electron spins in the sample can also give rise to line broadening. Dipolar interaction is a function of the reciprocal of the cube of the distance between the two dipoles, however, and with the small concentration of free radicals present in an irradiated sample, such interactions can be ignored.

Any processes by which the excited electrons lose their excess energy to the molecule or sample as a whole are known as spin–lattice interactions. If such interactions are strong, the lifetime of the excited spin state becomes very short and the uncertainty in the energy of the excited state then must increase in accordance with the uncertainty principle, causing an increase in the line width. The lifetime of the excited state is inversely proportional to the absolute temperature, so that cooling can be used to reduce this broadening of lines. Spin-lattice interactions take place through the mechanism of spin-orbital coupling. In free radicals the spin-orbital coupling is effectively quenched and spin-lattice interactions cause very little line broadening for these compounds.

The third factor influencing line width is again a result of the uncertainty principle, combined with the small size and indistinguishability of electrons. Exchange of electrons can occur between orbitals of different molecules, even when little chemical bonding is present between them. Such exchange interaction, as it is known, tends to smooth out the random internal fields experienced by the electron, resulting in a narrowing of the lines, and a change in the shape from Gaussian to Lorentzian.[30] Whenever the concentration of free radicals is high in a sample, this is an extremely important effect, and accounts for the very narrow lines observed for the spectra of naturally occurring free radical species.

Quantum Theory of Pi-Electron Radicals

Configurational Interaction

The spectra of organic free radicals are generally far richer in hyperfine structure and hence in information on molecular bonding, than the very basic theory thus far presented would indicate. Many of the free radicals which have been investigated are aromatic. The unpaired electron associated with such a planar ring system must be considered to be located in the pi-orbital system, so that delocalization will add to the stability of the radical through 'resonance', and hence the name pi-electron radicals. This configuration leads to the unpaired electron density being concentrated in regions out of the plane of the aromatic ring, and going to zero at any nucleus at the plane of the ring. Such an electron could have no interaction with any nucleus attached to the ring, and no hyperfine splitting could result.

Experimentally, aromatic free radicals do exhibit hyperfine splitting. The theory which has been developed to account for this apparent discrepancy is based on the fact that an excited state of σ-orbital character can be admixed with the ground state of pure π-orbital character. This effect is known as configurational interaction. Such interaction gives a finite density of the wave function of the unpaired electron spin at the nuclei attached to the ring, as well as at those forming the ring.

Conditions imposed upon the combination of the excited and ground state for configurational interaction to occur are that the states have the same symmetry with respect to reflection in the plane of the aromatic ring, and that the resulting state have the same spin multiplicity as the ground state. The ground state to be considered for a system of the unpaired electron, a ring carbon, and a nucleus, say a proton, bonded to it is $(\sigma_B)^2\pi$, (omitting filled orbitals), where σ_B is the bonding

orbital between the carbon and hydrogen. An antibonding orbital, σ_A, can be formed similarly to σ_B but with opposite signs of the overlapping carbon and hydrogen atomic orbitals. An excited state of the bond is formed if one bonding electron is promoted from σ_B to σ_A, thus giving $(\sigma_B)^1\pi(\sigma_A)^1$ as the excited state. Other possible excited states do not produce allowable combinations.

Mc Connell suggested[31] that the hyperfine splitting observed due to such concentration interaction is a direct measure of the unpaired electron distributions on the carbon atoms. The hyperfine splitting, a_n due to a proton attached to carbon atom N is then given by the simple formula,

$$a_n = Qq_n \tag{4}$$

where: Q is a constant for all aromatic hydrocarbons,

q_n is electron spin density at carbon at m N, and

$$\sum_n q_n = 2S \tag{5}$$

where: S is total spin.

Detailed treatments of configurational interaction applied to π-electron radicals have been carried out by Weissman[32], Jarrett[33], Bersohn[34], and McConnell with various co-workers[31,36-40]. The value of Q has been found semi-empirically to be -22.5 gauss for aromatic hydrocarbons. Theoretically it has been calculated to be -28 gauss.[33] In the admixing of the excited state with the ground state an effective partial unpairing of previously balanced orbits can result. Thus an extra odd electron spin density is produced in a direction opposite to that of the odd electron responsible for it. On some atoms then, q_n

may be negative[37,39]. The hyperfine splitting is independent of the sign of q_n, and the over all splitting due to the interacting hydrogens is written:

$$\sum_n |a_n| = Q \sum_n |q_n| \qquad (6)$$

Very good agreement with experimental results has been obtained by the use of this theory. It may be noted that although the summation over the spin densities in (6) can exceed one, it is usually close to one for aromatic radicals, and thus the total spread of the hyperfine spectra due to the ring protons is close to 23 gauss, independent of the number of protons interacting with the spin.

The theory of configurational interaction in hydrocarbons was specifically developed to account for the E.S.R. spectra of aromatic radicals. However, the development of the concept was far more general, being carried out by Mc Connell[37] in terms of a CH fragment. Thus the basic precepts may be extended to include any π-electron radical, that is to include the interaction of any proton bonded to a carbon on which the odd electron is considered to be localized in an orbit which has a node in the plane of the proton. Such a proton is known as an α proton.

Hyperconjugation

Experimentally it has been observed that in a methyl group bonded to an aromatic radical, the methyl hydrogens also can interact with the unpaired electron. Also the spectra of aliphatic radicals indicate that protons on the β carbon (that adjacent to the carbon on which the odd electron is localized) can have an interaction equivalent to that of α protons. Both of these effects are illustrations of the interaction

of β protons and since for such positions neither a multi-pi system nor an unbonded p_z orbital is available on the β carbon, configurational interaction as discussed above is not possible.

In the case of the aromatic radicals treated by configurational interaction considerations, the total spread of hyperfine lines from the ring protons was found to be very nearly constant regardless of the number of protons interacting. For aliphatic radicals on the other hand, the spread is very sensitive to the number of protons present, and indeed often appears almost directly proportional to it. To account for the observed large hyperfine splittings there must be some other mechanism for the odd electron wave function to include these various atoms. One means is through hyperconjugation.

Hyperconjugation depends on a spatial overlap of wave functions with the same pseudo-symmetry, and thus is a far more direct and potent effect than configurational interaction which depends on the interaction of electrons involving excited levels. Both calculations and experimental results bear out the truth of this.

Hyperconjugation can be explained in terms of valence bond (V.B.) or molecular orbital (M.O.) theory. Detailed discussions of hyperfine splitting due to hyperconjugation of methyl groups on aromatic free radicals have been presented in both V.B.[41] and M.O.[34] language. Coulson and Crawford[42] have presented a detailed analysis of hyperconjugation energies in toluene in terms of M.O. theory, and Chesnut[43] has followed this with a M.O. treatment of hyperconjugation leading to hyperfine splitting for the ethyl, isopropyl, and <u>t</u>-butyl radicals. The model discussed and the calculations set forth here are those of Chesnut.

M.O. theory requires that the electrons of the groups involved acquire a delocalization into orbitals of pi character. Considering as an example a methyl group, this delocalization is accomplished by treating H_3 as a single group, with ϕ_1, ϕ_2, and ϕ_3 indicating the 1 s atomic orbitals of the three hydrogens H_I, H_{II}, and H_{III} respectively. 'Group orbitals'[44] are then formed from these atomic orbitals. The approximate contours of the three group orbitals are shown in Figure 1.

The orbitals shown in I_b and I_c are closely similar to a normal pi-type orbital, that is there are regions of positive and negative ϕ with a nodal plane between similar to the nodal plane in a $2p\pi$ atomic orbital.

The three orthonormal group orbitals as given by Chesnut are listed in Table I, along with the methyl carbon atomic wave functions having similar symmetry.

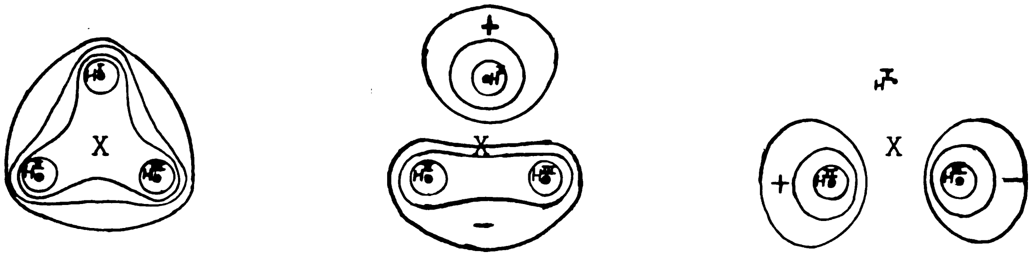
The bonding in a methyl group may then be pictured as follows: χ_1 forms a σ bond with one of the sp_1 hybrid orbitals of the carbon, the other sp_1 hybrid being free to bond to some other group; χ_2 and χ_3 form π bonds with carbon p orbitals p_2 and p_3 respectively.

The H_3 group can be considered as a pseudo-atom, and if the methyl group is bonded to a pi system, this pseudo-atom contributes one electron to the pseudo-pi or hyperconjugated system. The methyl carbon also contributes one electron to this pseudo-pi system.

The molecular wave function for this model is:

$$\Psi_\lambda = \sum_i c_{i\lambda} \psi_i \tag{7}$$

for the λth energy level. Each ψ_i in (7) refers to one of the normalized pi orbitals on one of the three types of atoms considered, that is,



I_a $\quad$ I_b $\quad$ I_c

$\phi_1 + \phi_2 + \phi_3$ $\quad$ $2\phi_1 - (\phi_2 + \phi_3)$ $\quad$ $\phi_2 - \phi_3$

Figure 1. Approximate contours of H_3 group orbitals. Orbitals are shown as in RCH_3 looking down the R-C bond indicated by X. (from Coulson,[44] p. 312).

Table I. Wave functions for group orbitals of H_3.

Group Orbital	Methyl Carbon Wave Function
$\chi_1 = \dfrac{\phi_1 + \phi_2 + \phi_3}{(3 + 6S_{HH})^{1/2}}$	sp_1
$\chi_2 = \dfrac{2\phi_1 - (\phi_2 + \phi_3)}{(6 - 6S_{HH})^{1/2}}$	p_2
$\chi_3 = \dfrac{\phi_2 - \phi_3}{(2 - 2S_{HH})^{1/2}}$	p_3
where $S_{HH} = \langle \phi_i \vert \phi_j \rangle$ $i \neq j$	

the α-carbon, the methyl carbon, and the pseudo-atom. The wave equation for the system is;

$$\mathcal{H}\Psi_\lambda = W_\lambda \Psi_\lambda$$

or

$$\sum_i c_{i\lambda}\mathcal{H}\psi_i = W_\lambda \sum_i c_{i\lambda}\psi_i \tag{8}$$

Each side of this equation is multiplied by the complex conjugates (ψ_i^*) of all orbital wave functions and integrated over all space. Collection of terms in the $c_{i\lambda}$ then gives the secular equations, (9).

$$\sum_{ij} c_{i\lambda}\int \psi_i^*\mathcal{H}\psi_j d\tau = W_\lambda \sum_{ij} c_{i\lambda}\int \psi_i^* \psi_j d\tau$$

or

$$\sum_{ij} c_{i\lambda}H_{ij} = W_\lambda \sum_{ij} C_{i\lambda} S_{ij}$$

$$\sum_{ij} c_{i\lambda}[H_{ij} - W_\lambda S_{ij}] = 0 \tag{9}$$

where

$$S_{ij} = \int \psi_i^* \psi_j d\tau = <\psi_i^*|\psi_j>$$

$$H_{ij} = \int \psi_i^*\mathcal{H}\psi_j d\tau = <\psi_i^*|H|\psi_j>$$

The energy of each level, W_λ, and the constants, $c_{i\lambda}$, can be determined by solving the secular determinant:

$$\text{Det} \left| H_{ij} - W_\lambda S_{ij} \right| = 0$$

Three assumptions are further made for the model: (i) overlap is neglected for all but neighboring atomic orbitals, (ii) the α-carbon atom is considered to be sp^2 hybridized, (iii) the resonance integrals,

H_{ij}, are taken as proportional to the corresponsing overlap integrals, S_{ij}.[45]

In writing the secular determinant, the terminology of Coulson and Crawford[42] is used. (Care must be observed due to the interchange of various symbols here among authors.[46])

$$S_{ij} = \langle \psi_i | \psi_j \rangle$$

$$H_{ii} = \langle \psi_i | H | \psi_i \rangle = \alpha + \epsilon_i$$

$$H_{ij} = \langle \psi_i | H | \psi_j \rangle \equiv \gamma_{ij} \equiv \rho_{ij}\gamma_0$$

$$\rho_{ij} = \frac{\gamma_{ij}}{\gamma_0} = \frac{S_{ij}}{S_0}$$

$$\beta_0 = \gamma_0 - \alpha S_0 \qquad (10)$$

β_0, γ_0, and S_0 refer to the values of these quantities for unsubstituted benzene.

Values must be assumed for S, γ, and also therefore for β. These all are functions of bond length, but can be related as above to comparable quantities for benzene.

The calculations to be made are illustrated using the ethyl radical. The pi centers are labelled as:

C^1-C^2-X^3 corresponding to $\cdot CH_2CH_3$

Two configurations of this radical are possible; the p_z orbital of C^1 can conjugate with the pseudo-pi system made up of p_2 and χ_2, or it can conjugate with that composed of p_3 and χ_3.

In considering the overlap of C^2 and X^3, it is apparent that;

$$\langle p_2 | \chi_2 \rangle = \langle p_3 | \chi_3 \rangle \qquad (11)$$

Thus either of these two configurations may be used equally well for the purpose of calculations. Chesnut chooses instead to consider each of the states as contributing equally to the true molecular state, that is, in effect he allows the methyl group to "rotate".

With the substitution of the quantities from (10), the secular determinant becomes:

$$\begin{vmatrix} \alpha + \epsilon_1 - W & \gamma_{12} - W\rho_{12}S_0 & 0 \\ \gamma_{12} - W\rho_{12}S_0 & \alpha + \epsilon_2 - W & \gamma_{23} - W\rho_{23}S_0 \\ 0 & \gamma_{23} - W\rho_{23}S_0 & \alpha + \epsilon_3 - W \end{vmatrix} = 0$$

or

$$\begin{vmatrix} \alpha + \epsilon_1 - W & \rho_{12}[\beta_0 + S_0(\alpha - W)] & 0 \\ \rho_{12}[\beta_0 + S_0(\alpha - W)] & \alpha + \epsilon_2 - W & \rho_{23}[\beta_0 + S_0(\alpha - W)] \\ 0 & \rho_{23}[\beta_0 + S_0(\alpha - W)] & \alpha + \epsilon_3 - W \end{vmatrix} = 0 \qquad (12)$$

It is assumed that the radical can be represented by a single electronic configuration, and that the lowest energy levels are filled in order, first with electron pairs, and then with the unpaired electron.

In order to obtain the eigenvalues and constants for the isopropyl and t-butyl radicals, the same secular determinant may be used if the ρ_{12} values are replaced by $(m)^{1/2}\rho_{12}$ where m is the number of methyl groups attached to the α-carbon atom, C^1.

In considering the Coulomb term for the pseudo-atom H_3, Coulson and Crawford[42] took cognizance of the o-p directing properties of a methyl group on benzene in electrophilic reactions. The migration of π electrons from the methyl group into the ring is indicated by this, and therefore H_3 must be considered to be more electropositive than C. This electropositivity is also shared somewhat with the neighboring C atom. This correction is to be found in the addition of ϵ_i to α, the Coulomb integral. The numerical values used for this correction, given in terms of the resonance integral for benzene, are :

$$\epsilon_1 = 0 \qquad \epsilon_2 = -0.1\beta_0 \qquad \epsilon_3 = -0.5\beta_0 \qquad (13)$$

These were chosen so as to reproduce the dipole moment of toluene, assuming it to be due to hyperconjugation.

Using Slater wave functions and $2p\pi$ overlap integrals, Crawford and Coulson calculated the value of S_{ij} as a function of bond length. The S_{ij} appropriate to the known interatomic distances in toluene and benzene were then used to determine the ratio designated as ρ_{ij}. The values used by Chesnut in his calculations are:

$$\rho_{13} = 0 \qquad \rho_{23} = 2.5 \qquad \rho_{12} = 0.7 \text{ and } \rho_{12} = 0.93 \qquad (14)$$

These are the rounded off values determined by Crawford and Coulson, with the exception of $\rho_{12} = 0.93$. This number is taken from Bersohn,[34] who obtained the best agreement between his theoretical calculations and the experimental results to which they were compared by the use of this value. Chesnut calculated his results using both values for ρ_{12}.

Since the overlap of adjacent atoms has been included in these calculations, the normalization condition for the molecular wave function becomes:

$$\begin{aligned} 1 = \langle \Psi_\lambda | \Psi_\lambda \rangle &= \sum_{ij} c_{i\lambda} c_{j\lambda} \langle \psi_i | \psi_j \rangle \\ &= \sum_{ij} c_{i\lambda} c_{j\lambda} S_{ij} \\ &= \sum_i c_{i\lambda} Y_{i\lambda} \qquad (15) \end{aligned}$$

where

$$Y_{i\lambda} = \sum_{j} c_{j\lambda} S_{ij} \qquad (16)$$

We are concerned with the energy level of the unpaired electron, which will be designated by a subscript zero. The odd electron density at an atom k, q_k, is given by [47,50]

$$q_j = c_{ko} Y_{ko} \qquad (17)$$

This definition requires, through the normalization condition, that the sum of the absolute values of all q_k is one. That is, spin densities are required to be positive. Since this is not necessarily true, as previously discussed, the theory is not a completely satisfactory one. Calculated values of q_k are shown in Table II.

The hyperfine splitting constants for the methyl protons only are calculated, using the Hamiltonian given in equation (3b). For a large applied magnetic field, only the interaction between the z components of electron and nuclear (those parallel to the field) need to be considered. Aside from a constant, the calculations reduce to the evaluation of,

$$\begin{aligned} \delta_s &= \langle \Psi_0 \,|\, \delta(\bar{r}_s) \,|\, \Psi_0 \rangle \\ &= \sum_{ij} c_{io}\, c_{jo} \langle \psi_i \,|\, \delta(\bar{r}_s) \,|\, \psi_j \rangle \qquad (18) \end{aligned}$$

where $\bar{r}_s$ is the distance from the s th proton to the electron, and

$\delta(\bar{r}_s)$ is the Dirac delta function.

Chesnut defines a function, Γ^s_{ij}, as the average of the term in angular parentheses, where

ρ_{12}

ρ_{12}

Table II. Results in the treatment of isotropic hyperfine interaction* through hyperconjugation for two values of the parameter ρ_{12}.

Radical	Coupling Constant $\lvert a_{me} \rvert$	Odd Electron Density q_c	q_x	$\frac{\lvert a_{me} \rvert}{q_c}$	$\frac{\lvert a_{me} \rvert}{q_x}$
$\rho_{12} = 0.70$					
Ethyl	16.9	0.9160	0.0815	18.48	207.6
Isopropyl	15.5	0.8433	0.0743	18.33	208.0
_t_-Butyl	14.2	0.7825	0.0684	18.19	208.2
$\rho_{12} = 0.93$					
Ethyl	27.8	0.8677	0.1307	31.99	212.4
Isopropyl	24.2	0.7669	0.1137	31.57	212.9
_t_-Butyl	21.5	0.6987	0.1008	31.17	213.4

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*D. B. Chesnut, J. Chem. Phys., 29, (1958), 45.

$$\Gamma^{s}_{ij} \equiv [\langle \psi_i | \delta(\bar{r}_s) | \psi_j \rangle]_{Av.} \tag{19}$$

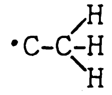
for example, $\Gamma^{s}_{23} = \frac{1}{2}[\langle p_2 | \delta(\bar{r}_s) | \chi_2 \rangle + \langle p_3 | \delta(\bar{r}_s) | \chi_3 \rangle]$

The averaging is required due to the earlier assumption of the 'rotating' methyl group, and has the effect of making all methyl protons equivalent, that is all $\bar{r}_s$ are equal. Calculations carried out by Chesnut show that the only elements of importance in the Γ matrix are those of the form Γ_{i3}. For the ethyl radical then, (18) reduces to,

$$\delta_s = \sum_i c_{io}\, c_{30}\, \Gamma_{i3}\, (2 - \delta_{i3}) \tag{20}$$

where δ_{i3} is the Kronecker delta.

The calculated elements of the Γ matrix, and the values used in the computation of these elements are listed below. Hydrogen-like wave functions were used:

for 

C-C distance = 1.54Å

C-H distance = 1.09Å

∠CCH = 109°28'

∠HCH = 109°28'

$\phi(0)$ = 1.4707

$(Z_{eff})_{hydrogen} = 1.00$

$(Z_{eff})_{carbon} = 3.25$

$\Gamma_{33} = 0.96580$ (21)

$\Gamma_{23} = 0.22050$

$\Gamma_{13} = 0.00811$

The energies calculated from (20) are related to the hyperfine coupling constants for the methyl protons, a_{me}. Rather than determining the value of the multiplicative constant in (3b), the absolute values of the a_{me} in gauss may be found using;

$$\left| a_{me} \right| = \frac{\delta_s}{\phi^2(0)} \, 506.2 \text{ gauss} \qquad (21)$$

where 506.2 gauss is the observed coupling constant for atomic hydrogen.

Table II lists the results obtained from this treatment of the three radicals.

Discussion

The approximations made in this rather simple M.O. treatment are admittedly crude, so that the exact numerical values listed in Table II are of small significance. However much of value is obtained in the way of general considerations about the coupling constants. The proper order of magnitude is obtained for the hyperfine splittings, which for such radicals are in the region of 20 gauss. The value of $\left| a_{me} \right|$ varies almost linearly with ρ_{12} in this region, and the choice of the value used for this parameter is quite arbitrary. Consideration of the selection of ρ_{12} based on Crawford and Coulson's calculations of S_{12} and S_0, shows that variation beyond the limits of 0.7 and 1.0 is doubtful. A value of $\rho_{12} = 1.0$ gives $\left| a_{me} \right|$ of about 31.5 gauss for the ethyl radical. Use of a comparison with experimental results as the criterion for selection of this value, as Bersohn did, is perhaps the best method. In any case, the results of the simple M.O. treatment do retain their order of magnitude correctness.

It is of great significance that the values of $\left| a_{me} \right|$ do not vary to any large extent among the three radicals considered, that is, with the addition of more methyl groups on the α-carbon atom. This corresponds to the observed fact that the total spread of the E.P.R. spectra of aliphatic radicals is roughly proportional to the total number of

protons interacting. The slight reduction in $|a_{me}|$ with an increasing number of methyl groups agrees qualitatively with the experimental results of Tsvetkov, Rowlands and Whiffen.[51]

In Table II the fifth column is seen to remain nearly constant among the three radicals, for a given value of ρ_{12}. That is to say, $|a_{me}|$ is roughly proportional to the odd electron density on the central carbon. As previously mentioned the splitting due to alpha protons has also been found to be proportional to q_{C_α}. Thus the couplings for the two types of protons, whose interactions result from mechanisms which apparently are totally different, 'accidently' become similar simple functions of the same quantity, q_{C_α} (Thus the need for 'artificial' radicals such as have been proposed[48] in the past is not necessary.)

The coupling constant for α protons on an sp^2 hybridized carbon has been estimated[49] as about -22(±5) gauss per unit of odd electron spin density from experimental data. The values of $\frac{|a_{me}|}{q_{C_\alpha}}$ from this M.O. treatment vary from 18 to 32 gauss. Due to the fairly large line widths occurring in the isotropic spectra of polycrystalline radicals, even quite large discrepancies in these values for the two types of protons might remain undetected. Thus the apparently equivalent interaction of chemically non-equivalent protons is completely within reason.

This simple theory is restricted to methyl hydrogens, and these constitute a special case, because of free rotation. In most cases[51] this free rotation can be verified down to a temperature of 77°K, and rotation has even been observed[52] to be nearly free in methylmalonic acid as low as 4.2°K. In one case[53], however, the rotation has been found to be quenched at 77°K. In most cases the beta protons of a methyl group are equivalent in interaction with the electron due to free rotation.

The more general cases of $R\text{-}\dot{C}H_2$, $R\text{-}\dot{C}H\text{-}R'$, and $R\text{-}\dot{C}\text{-}(R')R''$, have not been considered. For the general case, Heller and Mc Connell[53] have suggested that an expression for beta protons equivalent to equation (4) for alpha protons, should be of the form

$$a_{\beta} = R(\theta)\ q_{C_{\alpha}} \qquad (23)$$

where θ is the angle between the CH_{β} bond and the axis of the free radical p orbital as seen in projection in the plane perpendicular to the CC bond. The angular dependence of $R(\theta)$ is usually given the form:

$$R(\theta) = B \cos^2 \theta \qquad (24)$$

Thus any protons in the nodal plane of the p orbital occupied by the unpaired electron (this includes all alpha protons) cannot interact with the electron spin through hyperconjugation, and restriction of the rotation about the CC bond tends to change the coupling constants. In this way chemically equivalent protons can conceivably have non-equivalent interactions.

Several values for B have been suggested by various authors.[51,52,54-56] Heller and Mc Connell[53] originally suggested B = 40 gauss, considering the known interaction in $(CH_3)_2\dot{C}OH$. It is possible that B varies with the electronegativity of substituents. Attempts to locate the physical positions of beta protons through equation (24) have not been very successful due to the uncertainty in the value to be used for B. The equation can be used to qualitatively check values of coupling constants obtained for two non-equivalent beta-protons bonded to the same carbon, when the angle between them is known with some certainty.

Again in polycrystalline studies, the rather large line widths observed will hide small amounts of non-equivalence between protons. Where highly restricted bonds are present, the polycrystalline spectra may be difficult to interpret and the use of single crystal study necessary.

Characteristics of Hydrocarbon Electron Spin Resonance Spectra

The hyperfine interaction of organic radicals often exhibits anisotropy due to the strongly directed bonds present. The anisotropy is readily apparent in the electron spin resonance study of single crystals, in which spectra are taken as a function of the crystals orientation in the field. The hyperfine coupling of each nucleus to the unpaired electron can then be expressed as a tensor $\underline{A}$, which is symmetric in the absence of large spin-orbit intereaction. The trace of the tensor $\underline{A}$ is the isotropic part of the interaction, that which is observed for liquids and polycrystalline solids.

As shown in equation (3a), the anisotropic hyperfine interaction is proportional to r^{-3}. As a result, alpha- protons have a large anisotropy, but beta-protons show very little anisotropy, which allows a distinction to be made between them in single crystal studies. The effect of this in polycrystalline studies is an increase in line width when alpha-protons are present.[53,57] The greatest amount of information is obtained from the interaction of beta-protons, since this depends upon the physical position of the proton in the radical.[51]

Despite the great amount of information available from single crystals, the study of polycrystalline and liquid forms is most significant because they are so important physically, and, under certain

conditions, the isotropic spectra obtained from such samples can provide a considerable amount of information. After irradiation, whether by γ-rays, x-rays, ultraviolet light, neutrons, or electrons, a surprisingly large number of simple organic compounds do give simple electron spin resonance spectra. Combined with a knowledge of the structure of the parent compound, these spectra can usually be interpreted in terms of a single radical.

The problem of radical identification is considered in the light of some basic assumptions; the observed spectra are assumed to be related to simple radicals trapped in the system, and the structure of these radicals to be directly related to the structure of the parent compound. It is further generally assumed that only nuclei attached to the carbon on which the unpaired electron spin is concentrated and those on adjuacent carbons show interaction with the electron spin. That is, only α- and β-interaction is considered. The validity of these assumptions lies in the ability to interpret all spectra recorded within their limitations.

From the considerations in the theoretical discussion on beta-proton interaction, it is easy to understand that gamma-proton interaction would be very small, if it could occur at all. Hirota and Weissman[58] did succeed in observing a spectrum indicating the interaction of eighteen equivalent gamma-protons in the sodium and lithium ketyls of hexamethylacetone. The coupling constant observed for these protons was 0.12 gauss. Such a small coupling would certainly not be observed with the wide lines usually observed for polycrystalline solids.

Before discussing results of experiments, it is necessary to consider the nuclear spins of the atoms present in various compounds studied, and to determine the possible hyperfine patterns which might result. In hyperfine interaction with an unpaired electron, a nuclear spin I gives rise to a pattern of 2I + 1 lines of equal intensity.

Neither ^{16}O nor ^{12}C has a nuclear spin, and so these atoms cannot cause hyperfine splitting. ^{14}N has I = 1, which would result in a pattern of three lines of equal intensity. Since the compounds discussed contain one nitrogen at most, additive features need not be discussed. The ^{1}H nucleus has a spin of 1/2, giving a hyperfine doublet. If more than one hydrogen has an equivalent interaction with an unpaired electron, the effect can be determined by adding all possible combinations of the spins. For example, for two equivalent hydrogen nuclei, four combinations are possible: (1/2, 1/2), (1/2, -1/2), (-1/2, 1/2), and (-1/2, -1/2), giving total spins of 1, 0, 0, and -1 respectively, and resulting in a pattern of three lines of relative intensities of 1:2:1. In general, for n equivalent hydrogen nuclei, there are n + 1 lines in the hyperfine pattern, with relative intensities corresponding to the binomial coefficients. Both ^{35}Cl and ^{37}Cl have nuclear spins of 3/2, giving a pattern of four lines of equal intensity. Patterns for equivalent nuclei can be calculated as above. For two equivalent nuclei, seven lines result with relative intensities of 1:2:3$\overset{7}{:}$4:3:2:1. For the interaction of non-equivalent nuclei, or non-equivalent groups of equivalent nuclei interacting with the odd electron spin of a free radical, each line of the pattern having the larger splitting is further split into the pattern appropriate to the other nucleus or group. Such combinations may or may not overlap the various lines, but in general do contribute greatly to the complexity of the resulting spectrum.

Experimental results of some E.S.R. spectra from irradiated polycrystalline organic compounds which are ascribed to hydrocarbon free radicals are shown in Table III. (More comprehensive listings may be found in Ingram[10], pp. 166, 186 and 206.)

Some of the earliest work on irradiated aliphatic compounds was done by Gordy and his co-workers.[48] This group originally assumed that the simple, symmetrical spectra obtained which indicated equivalent proton interaction could be explained only in terms of a symmetrical molecular fragment, so that the odd electron would be in a non-localized, symmetrical M.O. covering the entire radical. They postulated that when the molecule is dissociated by the radiation an electron is removed, and whatever parts remain react among themselves to form the most stable assemblage of simpler molecules and radicals. Thus, such simple products as H_2O, NH_3, CO and CO_2 were assumed to be formed. The radical species they suggested were in general positive ion radicals. Observed quintets were ascribed to the ethylene radical, $(C_2H_4)^+$, and triplets to the methylene radical $(CH_3)^+$, or possibly to this group attached to some other. The single line they observed for irradiated formamide was attributed to $(CO)^+$, while the 5 line butyramide spectrum was interpreted as two triplets, but not explained.

A large variety of organic compounds have been irradiated using various radiation sources and the resulting E.P.R. spectra recorded. With this advance in the experimental data available, and the concurrent advance of the theoretical explanation of the observed spectra, it

Table III. Experimental results of some E.S.R. spectra from irradiated polycrystalline organic compounds.

Compound Irradiated	Type of Irradiation	Temp. °K	No. of lines	Peak Sep'n gauss	Total Spread gauss	Ref.
Methane CH_4	γ	20	4[a]	--	80	59
Ethane CH_3CH_3	γ	77	4x3	26[b]	79[c]	59
Propane $CH_3\text{-}CH_2\text{-}CH_3$	γ	77	8	25	175	59
n-Butane $CH_3CH_2CH_2CH_3$	γ	77	7	29	176	59
i-Butane $(CH_3)_2CHCH_3$	γ	77	(8)[d]	--	162	59
n-Pentane $CH_3(CH_2)_3CH_3$	e[e]	77	7	28	--	60
Neopentane	γ	77	10[f]	23	--	59
$(CH_3)_4C$			+3	24	--	59
n-Hexane $CH_3(CH_2)_4CH_3$	γ,e	77	7[g]	(29)	171	59,60
n-Heptane $CH_3(CH_2)_5CH_3$	e	77	7	(29)	--	60
n-Octane $CH_3(CH_2)_6CH_3$	e	77	7[g]	(29)	--	60
n-Nonane	γ	77	7[g]	--	166	59
$CH_3(CH_2)_7CH_3$	e	77	7[g]	(29)	--	60
n-Decane $CH_3(CH_2)_8CH_3$	e	77	7[g]	(29)	--	60
n-Undecane $CH_3(CH_2)_9CH_3$	e	77	7[g]	(29)	--	60
n-Octadecane $CH_3(CH_2)_{16}CH_3$	γ	77	6	33	165	59
n-Octacosane	γ	77	8[h] →	26	182	59
$CH_3(CH_2)_{26}CH_3$			6	31	157	
Polyethylene	γ	77	6	31	154	59
$(\text{-}CH_2\text{-})_n$	γ		7	--	90	61
Methanol	γ	77	3	18	36	59
CH_3OH	e	77	3	19	--	60
	x[i]	77	3	--	30	48
	u.v.*	77	3	17	--	62
	u.v.*[j]	77	3	19	--	63,64
Ethanol	γ	77	5	22	89	59
CH_3CH_2OH	e	77	5	22	--	59
	x	77	5	--	93	48
	u.v.*	77	5(10)*	(22)	--	63,64
	u.v.*	77	3+1	--	--	65

Table III (Cont.)

Compound Irradiated	Type of Irradiation	Temp. °K	No. of lines	Peak Sep'n gauss	Total Spread gauss	Ref.
n-Propanol	γ	77	(5or7)	20	80	59
$CH_3(CH_2)OH$	e	77	5	(18-20)	--	60
	u.v.*	77	5	23	--	65
	u.v.*	77	5	22	--	63,64
	u.v.	77	6	--	--	62
i-Propanol	γ	77	7	19.5	115	59
$(CH_3)_2CHOH$	e	77	7^m	(18-20)	--	60
	u.v.*	77	7	--	120	65
	u.v.*	77	7	20	--	63,64
n-Butanol	e	77	7	(18-20)	--	60
$CH_3(CH_2)_3OH$	u.v.*	77	7	20	--	63,64
	u.v.	77	6	--	--	62
s-Butanol	e	77	3^g	(18-20)	--	60
$CH_3CH_2CH(CH_3)OH$	u.v.*	77	6	21	--	63,64
	u.v.	77	6	--	--	62
i-Butanol	e	77	3	(18-20)	--	60
$(CH_3)_2CHCH_2OH$	u.v.*	77	8	23	--	63,64
t-Butanol	e	77	3^g	(18-20)	--	60
$(CH_3)_3COH$	u.v.*	77	3	24	--	63,64
n-Amyl alcohol	e	77	7	(18-20)	--	60
$CH_3(CH_2)$[illegible]OH	u.v.*	77	7	(18-20)	--	60
	u.v.	77	6	--	--	62
i-Amyl alcohol	e	77	(9)	(18-20)	--	60
$(CH_3)_2CH(CH_2)_2OH$	u.v.*	77	7	21	--	64
			+4	21	--	
t-Amyl alcohol $CH_3CH_2C(CH_3)_2OH$	u.v.*	77	5	22	--	64
n-Hexyl alcohol $CH_3(CH_2)_5OH$	e	77	7	(18-20)	-	60
Ethylene glycol	e	77	3^g	--	(10)	60
$OH(CH_2)_2OH$	u.v.*	77	3	--	--	65
Dimethyl ether	γ	77	3	--	35	59
$(CH_3)_2O$	e	77	3	(18-20)	--	60
Diethyl ether	γ	77	5	22	86	59
$(CH_3CH_2)_2O$	e	77	5	20	--	60
n-Propyl ether $(CH_3CH_2CH_2)_2O$	e	77	7	(18-20)	--	60
i-Propyl ether $(CH_3)_2CHOCH(CH_3)_2$	e	77	7^g	(18-20)	--	60
n-Butyl ether $(CH_3(CH_2)_3)_2O$	e	77	7	(18-20)	--	60

Table III (Cont.)

Compound Irradiated	Type of Irradi- ation	Temp. °K	No. of lines	Peak Sep'n gauss	Total Spread gauss	Ref.
Acetone $(CH_3)_2CO$	e	77	5	17	--	60
Methylethyl ketone $CH_3CH_2COCH_3$	e	77	5	(18-20)	--	60
Diethyl ketone $(CH_3CH_2)_2CO$	e	77	5	(18-20)	--	60
Diisopropyl ketone $(CH_3)_2CHCOCH(CH_3)_2$	e	77	5	(18-20)	--	60
Sodium methoxide	e	77	3	--	--	60
CH_3ONa	x	300	3	--	30	48
Formamide $HCONH_2$	x	77	1	--	--	48
Acetamide CH_3CONH_2	x	300	3	--	45	48
Propionamide $CH_3CH_2CONH_2$	x	300	5	--	98	48
Butyramide $CH_3(CH_2)_2CONH_2$	x	300	2x3	--	50^b	48
N-Ethylpropionamide $CH_3CH_2CONHCH_2CH_3$	e	195	5	--	--	66
N-Ethylbutyramide $CH_3(CH_2)_2CONHCH_2CH_3$	e	195	5	--	--	66
N-Ethylhexamide $CH_3(CH_2)_4CONHCH_2CH_3$	e	195	5	--	110	66
N-(*n*-Propyl)propionamide $CH_3CH_2CONH(CH_2)_2CH_3$	e	195	4	--	--	66
N-(*n*-Propyl)butyramide $CH_3(CH_2)_2CONH(CH_2)_2CH_3$	e	195	4	--	--	66
N-(*n*-Hexyl)propionamide $CH_3CH_2CONH(CH_2)_5CH_3$	e	195	4	--	121	66
N-(*t*-Amyl)propionamide $CH_3CH_2CONHC(CH_3)_2CH_2CH_3$	e	195	5	--	--	66
N-(*t*-Amyl)butyramide $CH_3(CH_2)_2CONHC(CH_3)_2CH_2CH_3$	e	195	5	--	135	66
N-(Neopentyl)propionamide $CH_3CH_2CONHCH_2C(CH_3)_3$	e	195	2+5	--	144	66
Methylamine CH_3NH_2	x	77	1	--	--	66
Acetanalide $CH_3CONHC_6H_5$	x	300	3	--	50	48
Tetra-*n*-butyl ammonium iodide $(CH_3CH_2CH_2CH_2)_4N^+I^-$	e	300	7	--	--	67

Table III (Cont.)

Compound Irradiated	Type of Irradiation	Temp. °K	No. of Lines	Peak Sep'n gauss	Total Spread gauss	Ref.
Tetra-n-nutyl ammonium bromide $(CH_3CH_2CH_2CH_2)_4N^+Br^-$	e	300	7	--	--	67
Nylon $(CO(CH_2)_4CONH(CH_2)_6NH-)_n$	γ	--	4	--	--	61
Propane 2,2-dicarboxylic acid $(CH_3)_2C(COOH)_2$	γ	300	7	22	--	51
2-Methylpropane-1,1-dicarboxylic acid	γ	300	89	23.5	--	51
$(CH_3)_2(CH)_2(COOH)_2$	x	300	89	23.5	--	51
2,2-Dimethylpropane-1,3-dicarboxylic acid $(COOH)CH_2C(CH_3)_2CH_2COOH$	γ	300	2	22.5	--	51
Cyclopentane-1,1-bisacetic acid $(COOH)CH_2C(CH_2)_5CH_2COOH$	x	300	2	21	--	51
Sodium cyclobutanecarboxylate $(CH_2)_3CHCOO^-Na^+$	x	300	5	32	129	51
Cyclobutane-1,1-dicarbosylic acid $(CH_2)_3C(COOH)_2$	x	300	5	32	--	51
Sodium cyclopentane carboxylate $(CH_2)_4CHCOO^-Na^+$	x	300	5	32	127	51
Ammonium-1,1-dimethylethane-1-carboxylate (ammonium trimethylacetate) $(CH_3)_3C-COO^-NH_4^+$	x	300	10	23	--	51

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[a] Intensities of lines are in the ratio of binomial coefficients unless otherwise indicated.

[b] Spacing between center lines of triplets.

[c] Spacing between the center lines of the outer triplets.

[d] Value given is uncertain.

[e] Irradiated with 2 Mev. electrons.

[f] Two radicals formed.

[g] Other lines present but not identified.

[h] Spectrum changes from the first listed to the second with increased time of irradiation.

[i] Irradiated with x-rays.

[j] Irradiated with ultraviolet light, primary radicals formed from dissolved H_2O_2.

[k] Observed occasionally.

[m] Intensities of lines are not in the ratio of binomial coefficients.

became apparent that a more probable explanation lay in rupture of a single bond by irradiation, with the products thus formed being trapped.[64] Although a C-H bond is stronger than a C-C bond the former is more often broken, perhaps due to the greater vibration occurring in a C-H bond. When a C-C bond is thought to be broken in a hydrocarbon the removal of a methyl group or a carboxyl group is almost always the result. Perhaps then the explanation lies in the size of the group removed. A small radical could readily escape through the lattice of the solid, while larger fragments, being trapped would tend to recombine. The simple removal of hydrogen or a methyl group during irradiation has considerable verification in chemical evidence.[69-73]

Smaller and Matheson[59] and Alger, Anderson, and Webb[60] surveyed the E.P.R. spectra of a large number of irradiated organic compounds of various classes, in the effort to characterize the spectra from particular types of radicals, and in an attempt to establish preferred points for bond rupture.

The spectra of all alkanes studied were shown to be consistent with the breaking of a C-H bond and removal of the proton. Smaller and Matheson were able to record the absorption due to the free hydrogen as well as that for the main radical. In general, the spectra indicated equivalent interaction of the spin of the odd electron with all alpha and beta protons. For ethane, however, Smaller and Matheson obtained a quartet of triplets, showing the slight non-equivalence of the 2 alpha and 3 beta protons. The small separation occurring here plainly demonstrates how this pattern might easily be overlapped to give a sextet if the lines were broadened through other effects. Their study of ethyl chloride and ethylene showed twelve-line spectra identical to that of ethane.

Normal propane, butane, hexane, and heptane give spectra consistent with the removal of a proton from a methylene group. The recurring appearance of 7 line spectra in the alkanes beyond propane indicates that the proton is removed specifically from the carbon next to the terminal methyl group. For higher alkanes other structure is observed in addition to the 7 line spectrum. The additional set of lines is not fully resolved, but Smaller and Matheson did identify it as an odd number of lines, which indicates it is not due to the formation of methyl or ethyl radicals, nor to the removal of a proton from the center of the chain, which radicals would give 4, 6, and 6 lines, respectively. Presumably radicals of the form $\cdot CH_2CH_2-$ are formed. The 6-line spectrum expected from radicals formed by the removal of a proton from the center of a polyethylene chain was observed for Marlex 50 (linear polyethylene) which has exceptionally low percentage of side chains. The 7-line spectrum obtained by Abraham and Whiffen[61] is undoubtedly due to proton removal from side chains present in their sample. The complex spectra obtained for branched alkanes indicate the presence of more than one radical. Apparently some breaking of C-C bonds does occur in these compounds.

The production of stable radicals from frozen alcohols irradiated with ultraviolet light is not readily accomplished. Some experimenters have used the alcohol as a solvent, dissolving in it H_2O_2 which easily forms radicals, probably $HO_2^{\cdot}$, which in turn attack the alcohol molecules, removing a proton and forming a secondary radical which is observed. Usually the same radicals are produced by this process as by the more common primary process.

In all cases irradiated alcohols give spectra indicating the removal of a proton from the hydrocarbon part of the molecule and the equivalent interaction of the remaining alpha and beta protons with the unpaired spin. No interaction with the hydroxyl proton is observed. As was observed for the alkanes mentioned above, the longer chain alcohols give seven-line spectra, indicating radicals of the type $-CH_2-\dot{C}H-CH_3$, and the complexity of the spectrum increases with branched compounds.

Two groups of investigators have carried out extensive studies on irradiated alcohols, studying both the effect of the length of irradiation and the temperature. Gibson, Symons, and Townsend[64] used ultraviolet light and dissolved H_2O_2, and were able to observe the formation of the primary free radical and then the secondary radical. The results of Fujimoto and Ingram[62] differ from those of others on the alcohols. The variation in experimental techniques may account for some of this. However, they were able to match their results theoretically by assuming radicals similar to those indicated by the results of others,[59,60,63-65] but taking into account also the effect of temperature on bond rotation, and the possibility of biradical formation.

The radical formed in the irradiation of n-propanol seems particularly to be in doubt. The need for more study on these simple compounds is clearly indicated.

Ethylene glycol gives a triplet spectrum[60,65] as would be expected if the C-C bond were broken but the spacing of this triplet is only about half that observed for a methyl radical.

The spectra of irradicated symmetric ethers follow much the same pattern, indicating that one proton is removed from one of the alkyl groups. n-Propyl ether again shows a five-line spectrum instead of the seven lines which might be predicted. No interaction across the oxygen is observed.

The spectrum resulting from acetone irradiated by a small dose of electrons is, surprisingly, a quintet.[60] Under continued irradiation and also under other conditions[68] a triplet is observed, such as would be expected if one C-H bond is broken. Assuming that the spin can only interact with atoms on the alpha and beta carbons, a five-line spectrum cannot readily be explained. Diethyl and methyl ethyl ketones both show five lines, indicative of proton removal from the ethyl group. The spectrum of diisopropyl ketone appears to be a quintet, but there is sufficient question about its form that the more likely seven-line spectrum is quite possible.

Burrell[66] used electrons to irradiate a series of amides. The E.S.R. spectra he obtained also indicated radical formation by breakage of a C-H bond. For N-substituted amides bond rupture preferentially occurs in the group bonded to nitrogen. Burrell found that a proton was usually removed from the CH_2 group adjacent to the nitrogen. If these positions are blocked, the proton is removed from the adjacent carbon. No interaction is observed across the nitrogen, that is, the other proton on the nitrogen does not interact. Only for N-(neopentyl)-propionamide was evidence of the presence of more than one radical found. One radical is apparently formed by proton removal from the carbon adjacent to the nitrogen, the other by proton removal from the carbon adjacent to the carbonyl.

Burrell[67] also studied tert-n-butyl ammonium halides. The seven-line pattern obtained from these salts indicates removal of a proton from the carbon in the beta position to nitrogen. This position for bond rupture was attributed to the increase in stability of the resulting radical due greater opportunities for hyperconjugation.

Single crystals of alphatic acids and their salts can readily be grown and upon irradiation they form radicals stable at room temperature in air. Therefore acids are usually studied in this form. Tsvetkov, Rowlands, and Whiffen[51] undertook a comprehensive study of these acids, and several fine individual studies[52-55,74-77] have appeared in the literature. Parallel investigation of some of these acids in both single crystal and polycrystalline forms have proven the fortunate circumstance that radiation damage gives the same radicals in both cases. This the more exact results from single crystal studies can be used to verify the information from the study of polycrystalline samples. In cases where the polycrystalline spectrum is a simple, fairly well resolved pattern, the single crystal spectrum is found to be generally quite similar and the radical identification from the former is correct. The results of a few cases of this type are shown in Table III.

From the large number of acids considered in single crystal form by Tsvetkov, Rowlands, and Whiffen, these authors were able to make a number of generalizations concerning the site of the electon spin in the stable radicals: (1) The α-carbon tends to be next to the carboxylic acid group and to have as few α-hydrogens as possible attached to it. (2) In no case was a proton removed from CH_3. (3) C-H bonds other than those in CH_3 break in preference to C-C bonds. (4) The C-C bond in C-COOH is more readily broken than that in $C-CH_3$. (5) Tertiary C-H bonds in $(C)_3CH$ break in preference to secondary C-H bonds in $(C)_2CH_2$ unless the CH_2 is adjacent to COOH. (6) In acids with more than two methylene groups, the radical often observed from other long chain compounds, $R-CH_2-\dot{C}H-CH_2-R'$, is not observed as the stable radical.

Abraham and Whiffen's[61] study of irradiated Nylon showed a four-line spectrum. This is consistent with the generalizations above and indicates that a proton is not removed from the center of a $(CH_2)_n$ chain.

EQUIPMENT

Introduction

The observation of electron paramagnetic resonance spectra may be accomplished by the use of a spectrometer such as is shown in the block diagram in Figure 2.

Such a spectrometer may conveniently be considered as four interdependent systems: (1) a homogeneous magnetic field and appropriate modulation of this field, (2) a system to measure the strength of the static magnetic field, (3) a system to generate and propagate microwaves, and (4) a system for the detection and display of the change of microwave power.

Two completely separate spectrometers were used in the experimental work discussed herein. The spectra taken previous to June, 1962, by S. K. Bolte and P. S. Rao were obtained using the spectrometer constructed at Michigan State University under the direction of Dr. M. T. Rogers, which is described in detail on pages 40-68. Spectra taken by K. R. Way after June 1962, were obtained using a commercial spectrometer described on pages 68-69.

The Spectrometer

The Magnetic Field

A magnetic field strength of roughly 3500 gauss is required to remove the degeneracy of the magnetic spin states in the irradiated compounds used. In order to obtain this field, an electromagnet which had

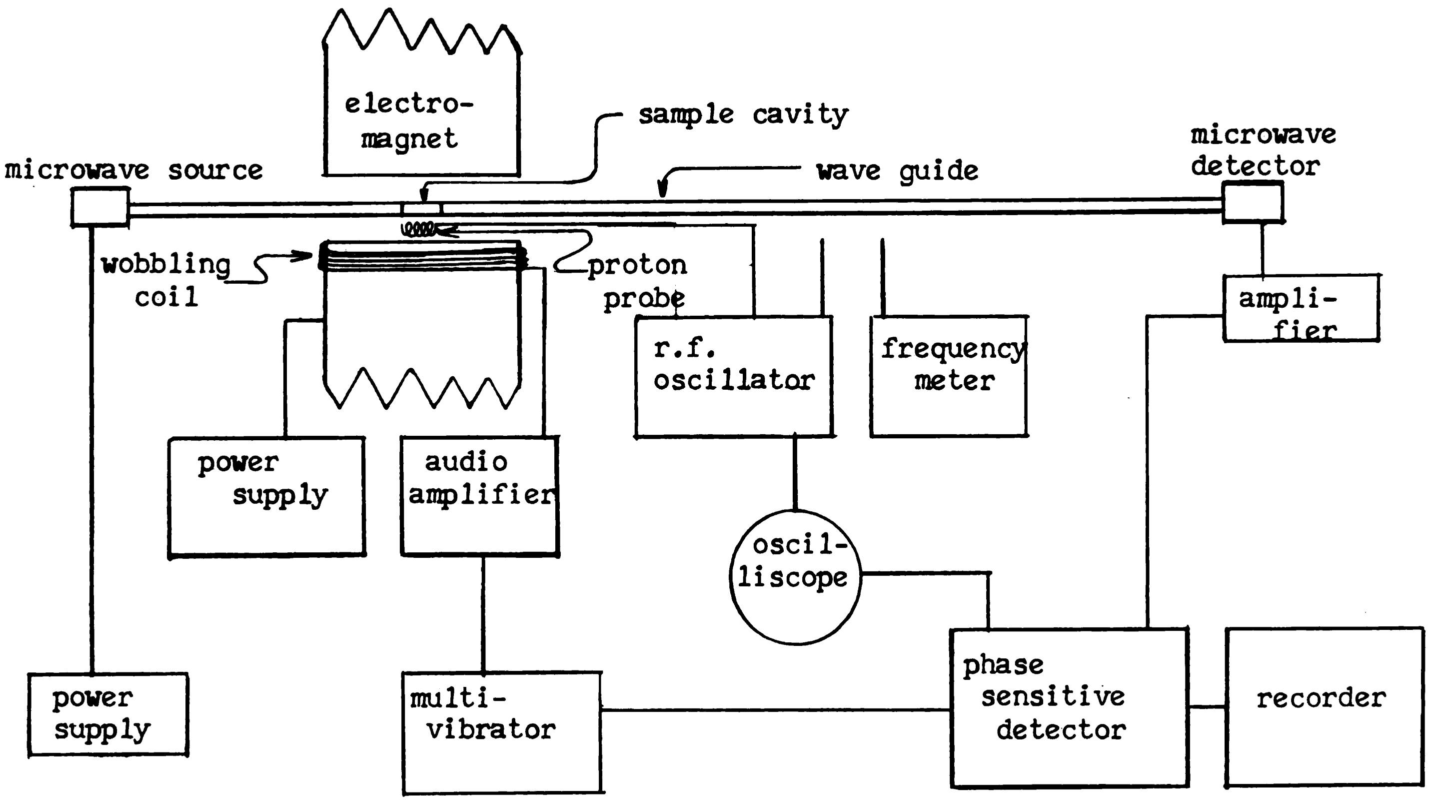

Figure 2. Block diagram of an E.S.R. spectrometer.

been constructed under the direction of M. T. Rogers, H. B. Thompson, and J. R. Faber was used.[78,79] The electromagnet consists essentially of six copper spools with approximately 1200 turns of Formvar insulated #14 copper magnet wire on each spool. Three spools are placed around each 7 1/2 inch pole piece. The three coils on each side are wired in series and the leads brought out to the terminal box on the magnet mount. The total from the two sides gives roughly 23,000 feet of wire, with a resistance of 50 ohms. In order to increase the homogeneity of the magnetic field, the original 7 1/2 inch pole caps were replaced by a pair of 12 inch pole caps removed from a Varian* N.M.R. spectrometer. Two sheets of 1/2 inch aluminum were suitably machined so as to fit between the pole pieces and rest on the magnet mount. Circular areas were machined out of the center of these sheets, so that the existing pole pieces could extend through the aluminum sheets. To these sheets, the 12 inch pole caps were bolted. At each of the four corners of the aluminum sheets, turnbuckles were placed joining the two, thus holding the structure rigid. These turnbuckles were adjusted until the most homogeneous field possible was obtained. At all times the pole pieces were kept tight against the pole caps, by using the handwheels and threaded steel rod extending into the pole pieces, as built into the original design of the magnet. The homogeniety of the field was determined by recording the E.S.R. line of a solution of sodium dissolved in liquid NH_3. This line is reported by Hutchison[80] to be 0.02 gauss wide. The minimum width recorded on this spectrometer was 0.2 gauss. The setting of the turnbuckles used to obtain this minimal width was assumed to give the best homogeneity and was thus used during succeeding experiments.

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*Varian Associates, Palo Alto, California.

The power supply for the electromagnet is shown in Figure 3. The local 220 volt three-phase power supply is converted into direct current, using a three-phase bridge of selenium rectifiers as shown in Figure 3a. The rectifiers are cooled by means of a fan.

This bridge is able to deliver 250-300 volts at up to 25 amperes. The pulsed, rectified current is next fed into a series of inductance-capacitance filters which smooth out most of the ripple. However, the remaining ripple is still too great for the desired steady field. The current is therefore next fed into a current regulator which both minimizes current fluctuation and provides the means by which the magnetic field is swept.

The magnetic coils are in the cathode circuit of the 6L6 power tetrodes. The 6L6's are placed in parallel on 5 chassis, holding 18 tubes each. The screen grid voltage for the 6L6's is obtained from a separate fixed-voltage regulator circuit. (Figure 3c.)

Coarse selection of the current range for the magnet coils is provided through a choice of contact points on the dropping resistance between the coils and the negative input. This dropping resistor is a hand-wound, water-cooled coil of nichrome wire, providing a precision resistor little affected by temperature changes.

Sweep of the chosen magnetic field region is provided by a motor-driven Helipot[*] potentiometer which is in parallel with a portion of the dropping coil (See Figure 3d.)

The 1μf and 16 μf capacitors smooth out current fluctuations across the magnet. To eliminate any fluctuations due to another external power source, batteries were used on the screen grid and cathode of the 6AU6.

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[*] Beckman Instruments, Inc., Helipot Division, Fullerton, California.

Any fluctuation in potential causing an increase in current through the magnet causes a positive excursion of the control grid of the 6AU6, thus increasing its conductance. This results in a negative excursion of the grids of the 6L6's, decreasing their conduction, and also the current through the magnet.

In order to modulate the magnetic field, a modulation or 'wobbling' coil was wound around one of the 12 inch pole caps. To decrease vibration, the pole cap was first covered with a layer of rubber mat, and then wound with foam rubber. The coil was wound of lacquer-coated flat copper wire having a cross sectional area equivalent to #18 wire. The coil was wound in six layers, ten turns in each layer, the layers being separated by a covering of masking tape. The leads to this coil were run to the terminal board on the side of the magnet yoke.

The wobbling coil is energized by a square-wave signal obtained from the non-sinusoidal oscillator, or astable multivibrator shown in Figure 4. A condition of instability is caused by slight differences in the plate currents of the two halves of the first 6SN7. The positive feedback network between these two sections supports this tendency toward instability, giving a very rapid transition in which the grid of one section is driven below cutoff, the other half simultaneously going to full conduction. The transition occurs when one plate, say the one on the left, tends to go positive, causing the right-hand grid also to become more positive. Thus conduction in the right-hand side increases causing that plate to become more negative and producing a negative excursion of the grid on the left. This results in the left-hand plate becoming even more positive. This tendency rapidly increases until the left side reaches cutoff, the right side conducting fully. When this happens the charges on C and C' in the plate circuits leak off slowly to ground. During this process the conduction of the right side slowly decreases, and conduction on the left side begins again when the grid potential is sufficiently raised. When the two sections are conducting equally again, the circuit is again triggered with the left side going to full conduction this time. This oscillation between cutoff and full conduction alternately in the two halves continues. The rate at which the charges leak off to ground is a function of the time constant of the resistance-capacitance (R.C.) networks. Therefore the output frequency of the multivibrator can be adjusted by the insertion of various values of C and C'. In use the multivibrator was adjusted to oscillate at 112 cps. The signal from one cathode of the 6SN7 is amplified by a 6SJ7, and the amplified signal fed to two cathode follower outputs.

One signal from the multivibrator is fed into the audio amplifier shown in Figure 5. A 6SL7 divides this input, providing proper signals for push-pull operation of the two 6L6 tetrodes (180° out of phase), the plates of which are connected to an output transformer. These lead directly to the wobbling coil terminals. The proper amplitude and wave form of the wobbling coil current are obtained by variable attenuation of the signal from the multivibrator as it enters the amplifier. The maximum current obtainable in the coils is 2.5 amperes.

Measurement of the Magnetic Field

An accurate and conveneint measurement of the magnetic field may be made by the use of the N.M.R. resonance frequency of the proton, which is given[81]by

$$\upsilon_p = 4.2577H \times 10^3 \text{ cps} \qquad (25)$$

Use is made of the wide-range marginal oscillator described by Buss and Bogart.[82] This circuit was developed by those authors for use at frequencies below 25 Mc/sec, and is particularly suitable for the case where it is necessary to insert several feet of coaxial cable between the oscillator and the probe, as in this E.S.R. Spectrometer. The circuit used is shown in Figure 6. Power for the oscillator is obtained from a Lambda* regulated power supply, Model 28.

A very dilute solution of manganous sulfate in distilled water is placed in the probe coil of this oscillator. The probe is inserted between the pole caps with its axis perpendicular to the magnetic field, and as close as possible to the sample. The variable capacitor is used to set the desired frequency of oscillation in the resonant circuit, which includes the proton probe. The crystal in this circuit stabilizes the frequency. Frequencies set on this oscillator are in the radio frequency range. When the magnetic field, as modulated by the wobbling coils, reaches the point of proton resonance, energy from the resonant circuit in the oscillator is absorbed by the water sample in the probe, decreasing the oscillator output amplitude. The oscillator output is therefore periodically decreased at a frequency corresponding to the period of the wobbling coil current, i.e. 112 cps. The output of the oscillator feeds into a low-pass filter, giving an input signal to the amplifier, (V_3), with amplitude variations at 112 cps. The output of the amplifier is impressed on the vertical plates of an oscilloscope which is synchronized to 112 cps., giving a positive-going pulse at the

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*Lambda Electronics Corp., Huntington, Long Island, N.Y.

point of proton resonance absorption. V_2 acts as an impedance-matching device between the oscillator and the frequency check point. The frequency may be rapidly determined to an accuracy of five significant figures by the use of a type BC-221-O United States Army Signal Corps frequency meter.

Microwave System

The microwave power is generated by a Varian X-13 or V260 reflex klystron, which is capable of generating microwaves in the frequency range of 8.2 - 12.4 kmc. This type of klystron is normally operated with the tube body (the anode) at ground potential. The cathode then operates at -450 volts, and the repeller at about 450 volts negative with respect to the cathode. The beam current is about 50 m.a.

The cathode voltage is supplied by a voltage-regulated power supply. The circuit diagram of this supply, Figure 7, shows it to be essentially composed of a D.C. supply, a filter network and a voltage regulator. The input to this power supply is, in turn, from a Sorenson* model 500S voltage regulator.

In order to insure a constant voltage difference between the cathode and the repeller, a battery high-voltage source was used between these two, the voltage applied being variable by means of a series of switches (Figure 8). This voltage source includes a 90-volt battery which is always in the circuit, thus preventing the repeller from having a voltage positive with respect to the cathode.

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* Sorenson and Co., Inc., South Norwalk, Connecticut.

In order to reduce drift in the klystron frequency due to temperature variation, the tube was immersed in a circulating bath of oil.

Transmission of the microwaves is accomplished by the use of type RG·52/U waveguide. Coupling between the various components in the wave guide train is made with type UG-39/U flanges and type UG-40/U chokes.

Directly after the klystron in the microwave line, a Uniline* Microwave Gyrator, model 88-96B is inserted. This isolator allows the radiation to pass through in a forward direction, but attenuates any radiation which might be reflected and which, if allowed to pass, would throw the klystron off its set frequency.

A Waveline** Attenuator, type 611, is placed next in the microwave line. This allows variation of the microwave power delivered to the sample, to obtain a sufficiently large spectrum for study, and to avoid saturation.

Suitable lengths of waveguide then transmit the microwaves to the cavity within the magnetic field, and on to the detection systems on the other end.

The microwave power transmitted through the microwave system is indicated by an MA-423A crystal diode, mounted in a tunable crystal mount, Hewlett-Packard*** Model X-485B.

Between the sample cavity and the detector crystal diode, a directional coupler is placed. This coupler leads to a Waveline 698 wavemeter,

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* Cascade Research Corp., Los Gatos, California.

** Waveline Inc., Caldwell, New Jersey.

*** Hewlett-Packard Co., Palo Alto, California.

and then to a termination. This wavemeter was used to determine the frequency of the generated microwaves. The wavemeter was calibrated against another system for the measurement of klystron frequency, which was known to have an accuracy of ± 0.5 mc. This system was composed of a Gertsch[*] FM-4A and AM-1A beating a standard frequency against the klystron frequency, with the frequency difference measured on a Hallicrafter[**] 5X-62A receiver. The error in the wavemeter was found to be of the order of ± 0.5 mc, with a maximum error of ± 1 mc. In the 10 kmc region used, this error is about 1 part in 10^4. A further measurement was made using diphenylpicrylhydrazyl (DPPH) as a standard having an absorption line of known frequency at a given field. The wave meter was found to give a frequency reading to an accuracy of 0.055%.

Signal Detection and Display

The electrical signal produced by the detector crystal diode as a result of the microwave power impinging upon it, is immediately amplified by the use of a small preamplifier with a wide band pass. This preamplifier is mounted directly on the crystal at the end of the wave guide in order to reduce noise from a lead. This preamplifier is a two stage amplifier followed by a cathode follower with a negative feedback loop to the first stage. This feedback increases stability and decreases noise. The circuit diagram is shown in Figure 9. Power for the preamplifier is obtained from the power supply for the phase-sensitive detector (Figure 10). The output from the preamplifier is fed into the phase-sensitive detector.

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[*] Gertsch Products Inc., Los Angeles, California.

[**] Hallicrafters Co., Chicago, Illinois.

Due to the use of 'wobbling coils' in this system, the magnetic field is being modulated during its sweep across the absorption region. The microwave power received at the crystal is at a constant level, except when the magnetic field is such as to cause absorption. In that region, the power is decreased and is modulated at the same frequency as the wobbling coil current, 112 cps. The amplitude of the modulations as received at the crystal is proportional to the first derivative of the absorption peak, going to zero at the point of maximum absorption and reversing in phase on the return (upward) slope of the line.

The phase-sensitive detector is used to amplify that part of the received signal which is modulated at 112 cps., shift the phase of this signal to match that of a reference signal from the multivibrator, and give an output the amplitude of which shows the amplitude and phase of the 112 cps. signal from the preamplifier. The circuit diagram of the phase-sensitive detector is given in Figure 11.

The signal from the preamplifier enters the phase-sensitive detector through an attenuator switch and onto one grid of V_1, which acts as an impedance-matching device. The signal is next amplified by V_2, the plate of which is connected to the gain control potentiometer. The signal then is fed into the grid of V_{3a}, used as cathode follower, coupling the signal into a twin-tee amplifier circuit, which contains V_4, V_{3b}, and a twin-tee filter. The signal is amplified by V_4 and then appears on the grid of V_{3b}. The signal is further amplified at the plate of V_{3b} and fed on to the next section of the circuit. At the same time the signal from the cathode of V_{3b} is fed back through the twin-tee filter to the control grid of V_4. The twin-tee is so constructed as to present a low impedance to all frequencies except those in a narrow band centered about the desired frequency, here 112 cps. Thus all signals are cancelled out at V_4, except those in the band about 112 cps. Design of the twin-tee filter is given in Figure 12.

The output of the frequency selector section of the phase-sensitive detector is fed into two phase-shifting circuits, each capable of a phase shift of nearly 90^0. The phase of the signal coming out of these circuits is dependent upon the values of resistance and capacitance in the R-C networks in the output circuits of V_{5a} and V_{5b}. Coarse phase control is obtained by switching in capacitors of various values, fine control by varying the resistance.

The output of the phase-shift section of the phase-sensitive detector is coupled through an isolation amplifier, V_6, to both cathodes of V_7. At the same time a 112 cps reference signal from the multivibrator is fed through a buffer amplifier (V_{8a}) and direct-coupled to the grid of a phase splitter (V_{8b}). The two signals, equal in amplitude and frequency, but opposite in phase, which are then obtained from the plate and the cathode of V_{8b} are applied to the two grids of V_7, so that each half of V_7 conducts alternately for one half cycle.

With no absorption signal, the two plates of V_7 will be at the same potential. Exact balance in the plate circuits of V_8 is obtained by a variable resistance between the two plates. This is the D.C. balance control. The signal applied to the cathode of V_7 is adjusted to be exactly in phase with the reference signal. During absorption the signal on the cathode will be in phase with the signal on one grid, and 180^0 out of phase with the signal on the other grid. The half-tube with signals out of phase will increase in conductance, the other half will decrease in conductance. Thus the two plates of V_7 will be at different potentials, the amount of difference being proportional to the amplitude of the signal, and the sign of the difference being dependent upon the phase of the signal.

The output from the plates of V_7 is fed through an R.C. filter network to V_9 which acts as a vacuum-tube voltmeter, the output of which drives both a meter movement and a recording potentiometer. The time constant of the R.C. network is adjusted by switching various values of capacitance into the circuit. A large time constant reduces the noise level of the output signal. However, this creates the possibility of distortion or loss of the fine structure in the spectra unless care is taken to keep the sweep slow enough that the circuit is able to respond.

The spectrometer has an alternate system of display, known as crystal video detection. In this case the output of the preamplifier is fed directly to the Y plates of an oscilliscope. The sweep of the oscilliscope is synchronized with the modulation field sweep. At the condition of resonance, the entire absorption spectrum is traced out on the oscilliscope screen. For this display system to be used, the amplitude of the field modulation must be large compared to the spread of the spectrum, so that it sweeps through all of the absorption pattern twice per cycle of modulation. This system of detection is of considerably lower sensitivity than the phase-sensitive detection and pen-recorded display. A polaroid camera can be used for a permanent record of the oscilliscope spectrum.

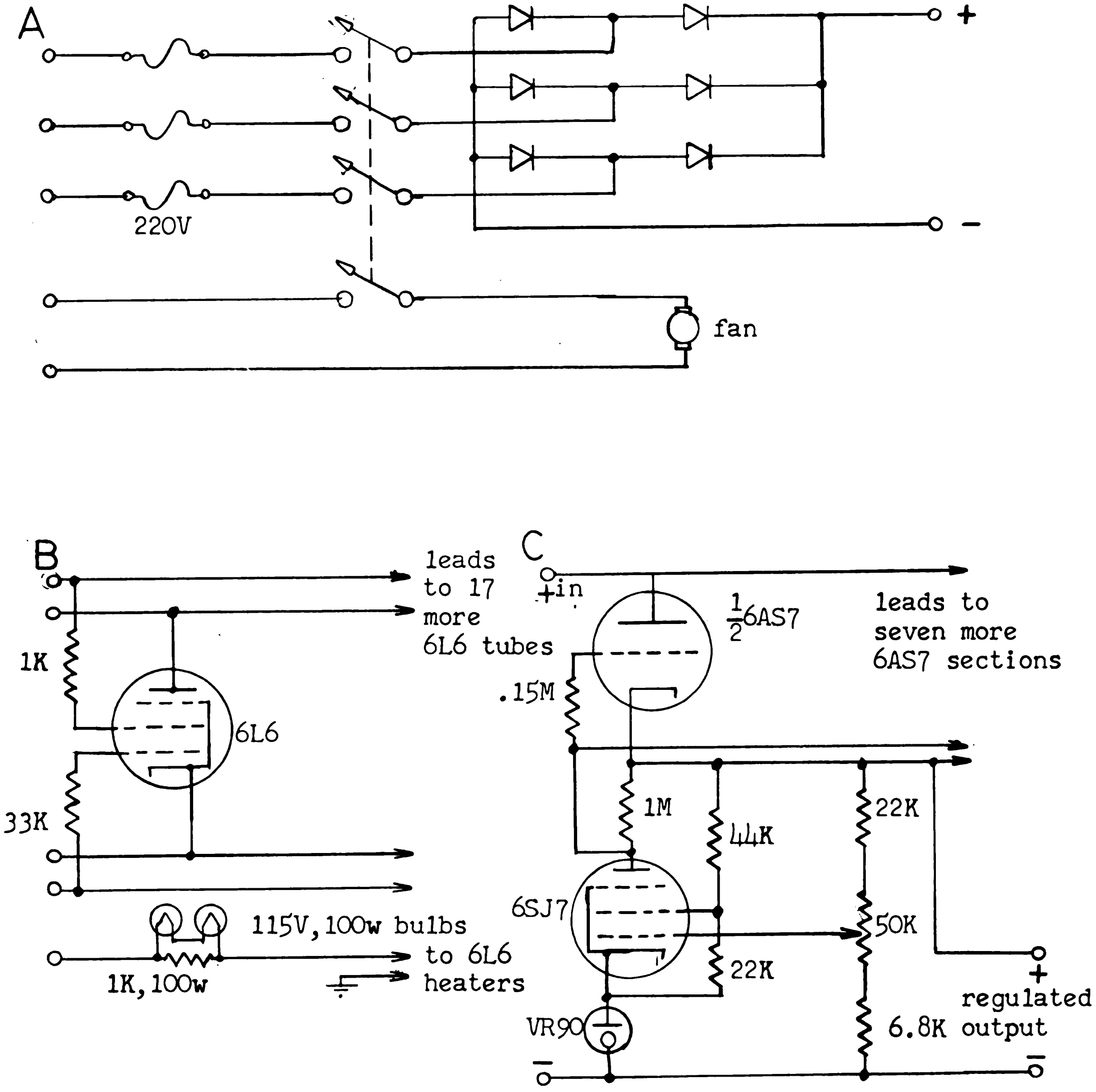


Figure 3. Circuit of power supply for the electromagnet: A. Three phase bridge. B. Circuit of one of the five banks of 6L6 tubes. C. Voltage regulator circuit for screen grids of 6L6 tubes.

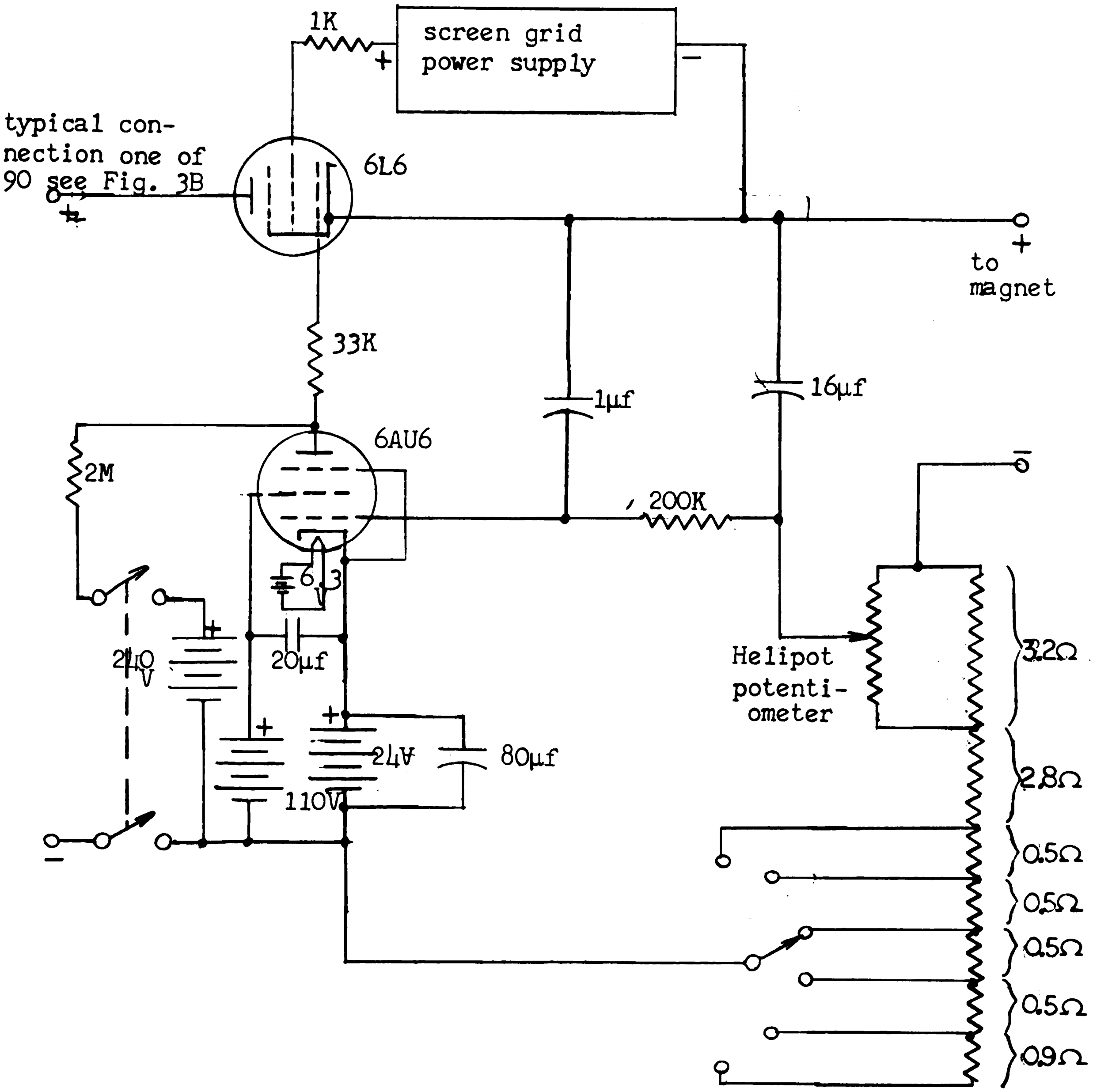


Figure 3 (Cont.). D. Circuit of the magnetic field sweep unit.

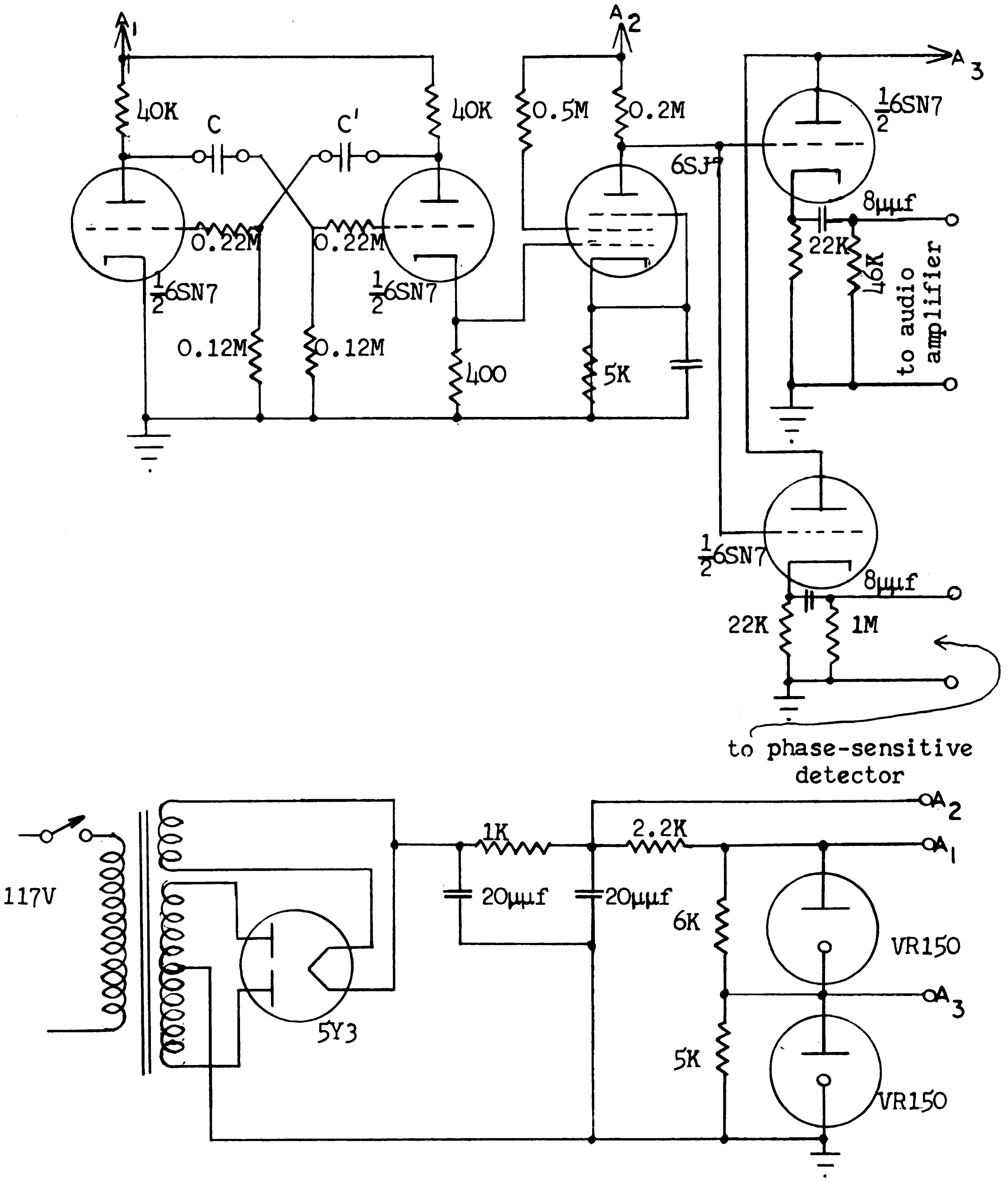


Figure 4. Circuit of multivibrator and its power supply.

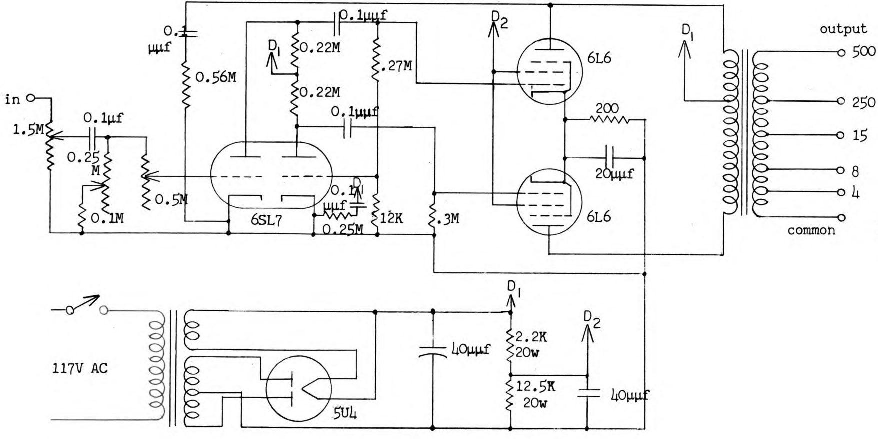


Figure 5. Circuit of the audio amplifier.

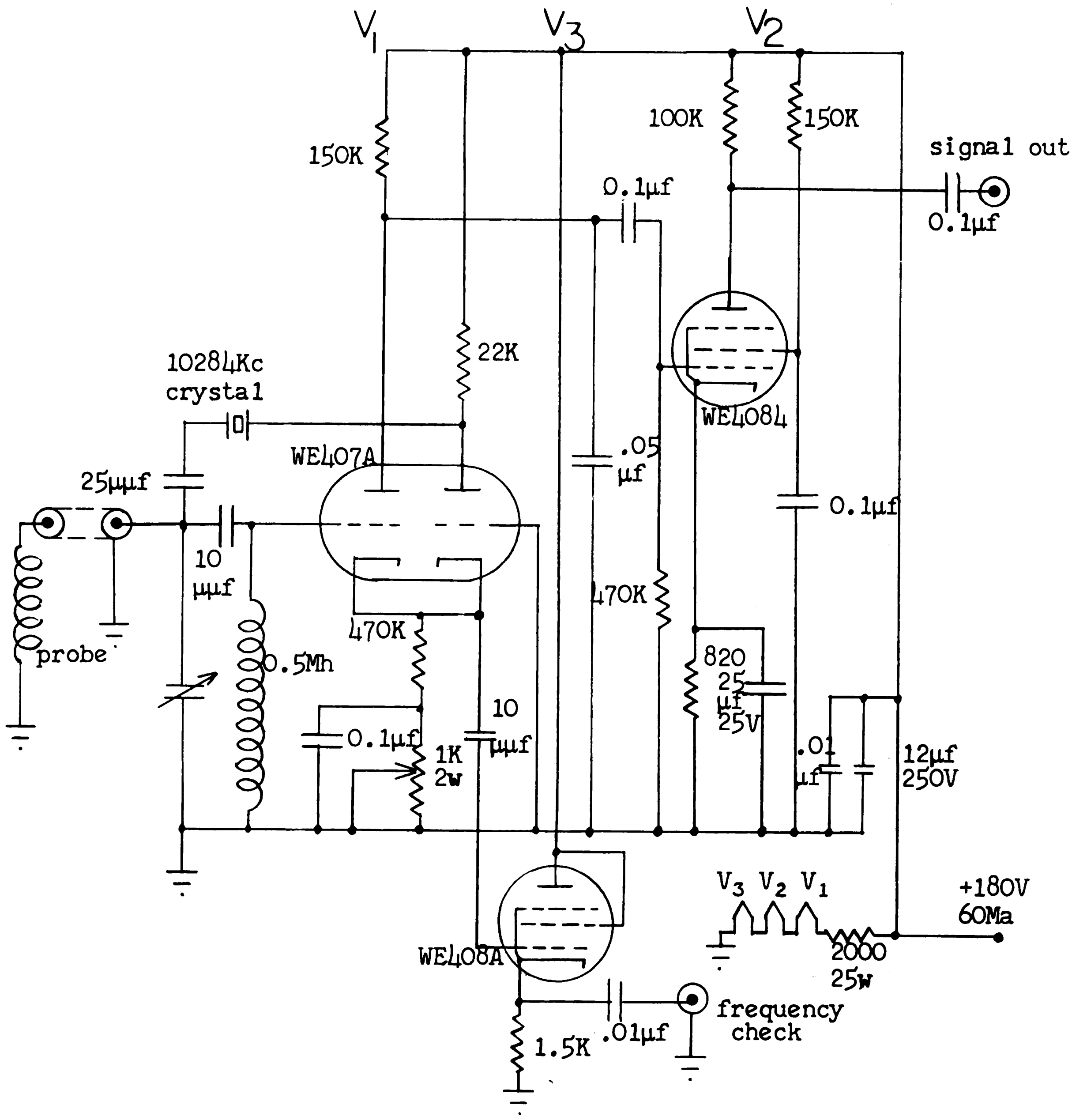


Figure 6. Circuit of the proton frequency meter.

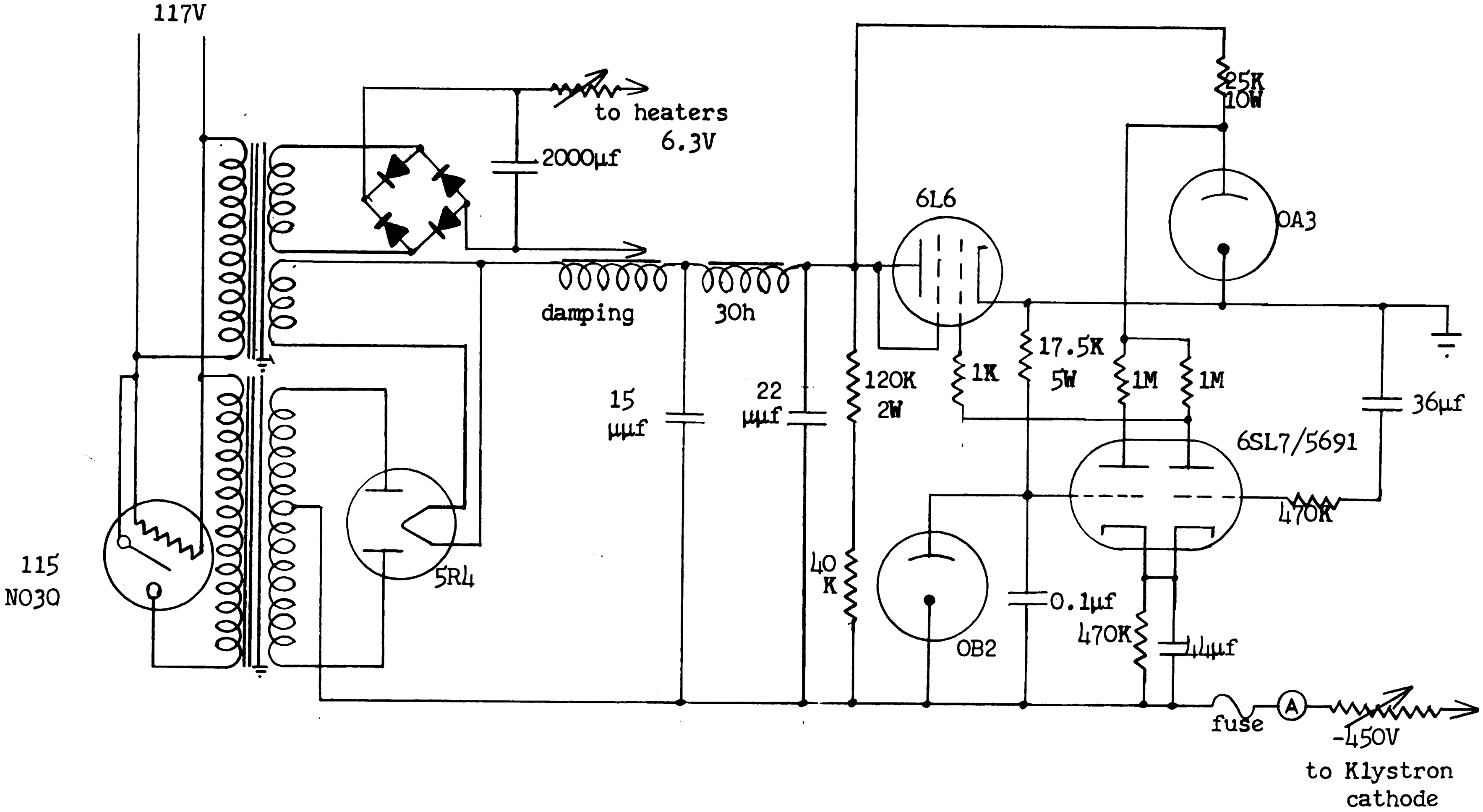


Figure 7. Circuit of the low voltage Klystron power supply.

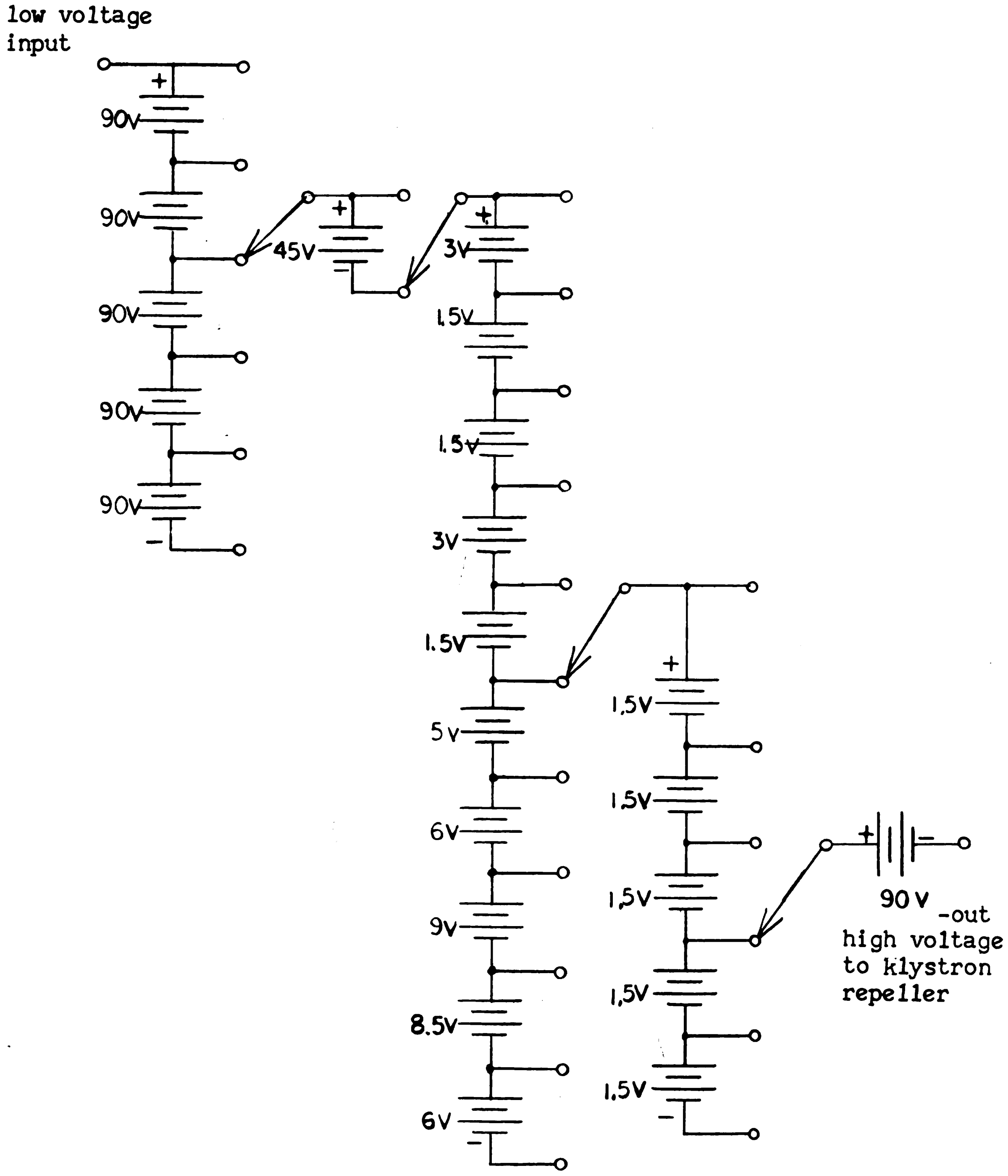


Figure 8. Circuit of the battery high voltage klystron power supply.

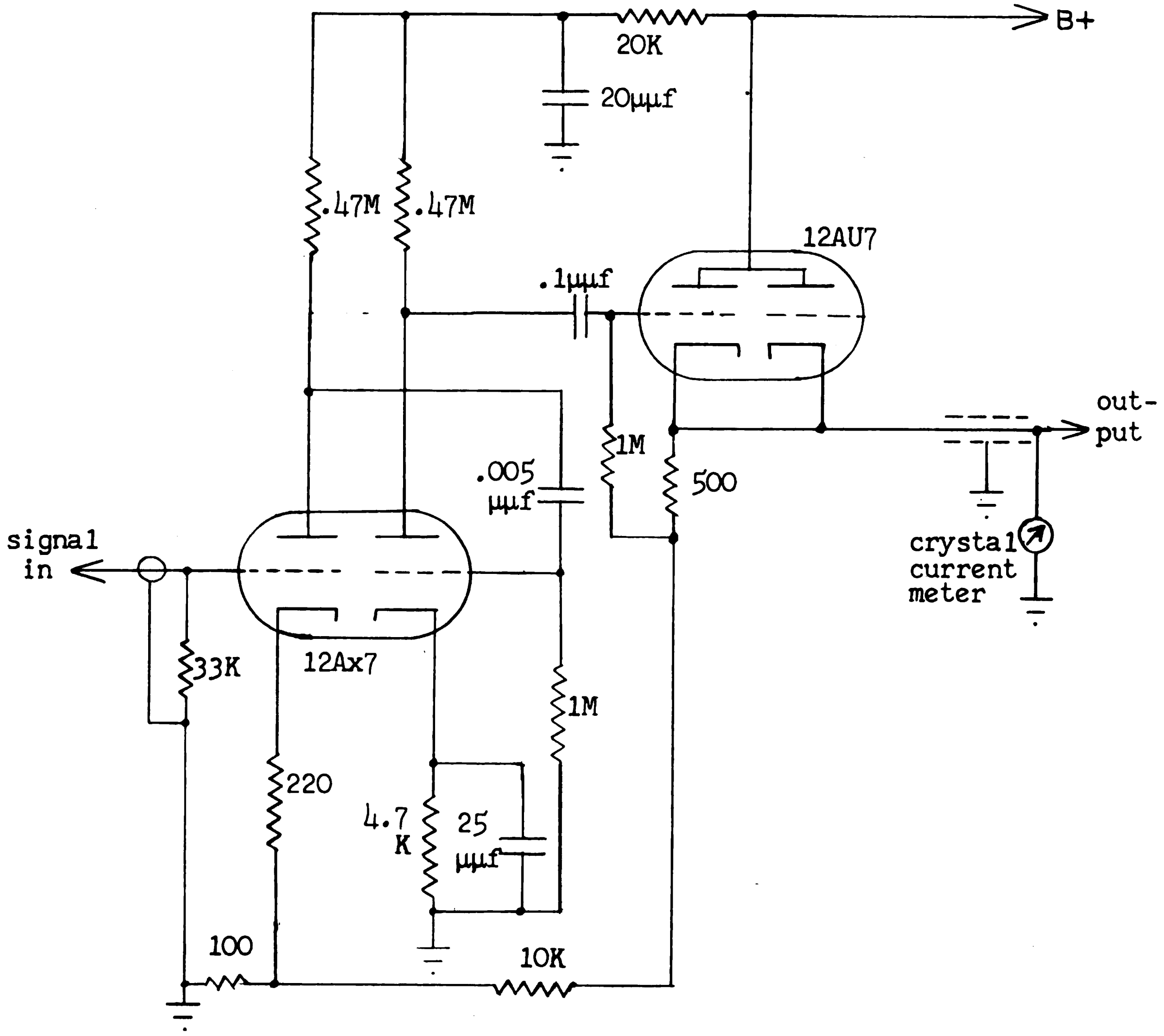


Figure 9. Circuit of the preamplifier.

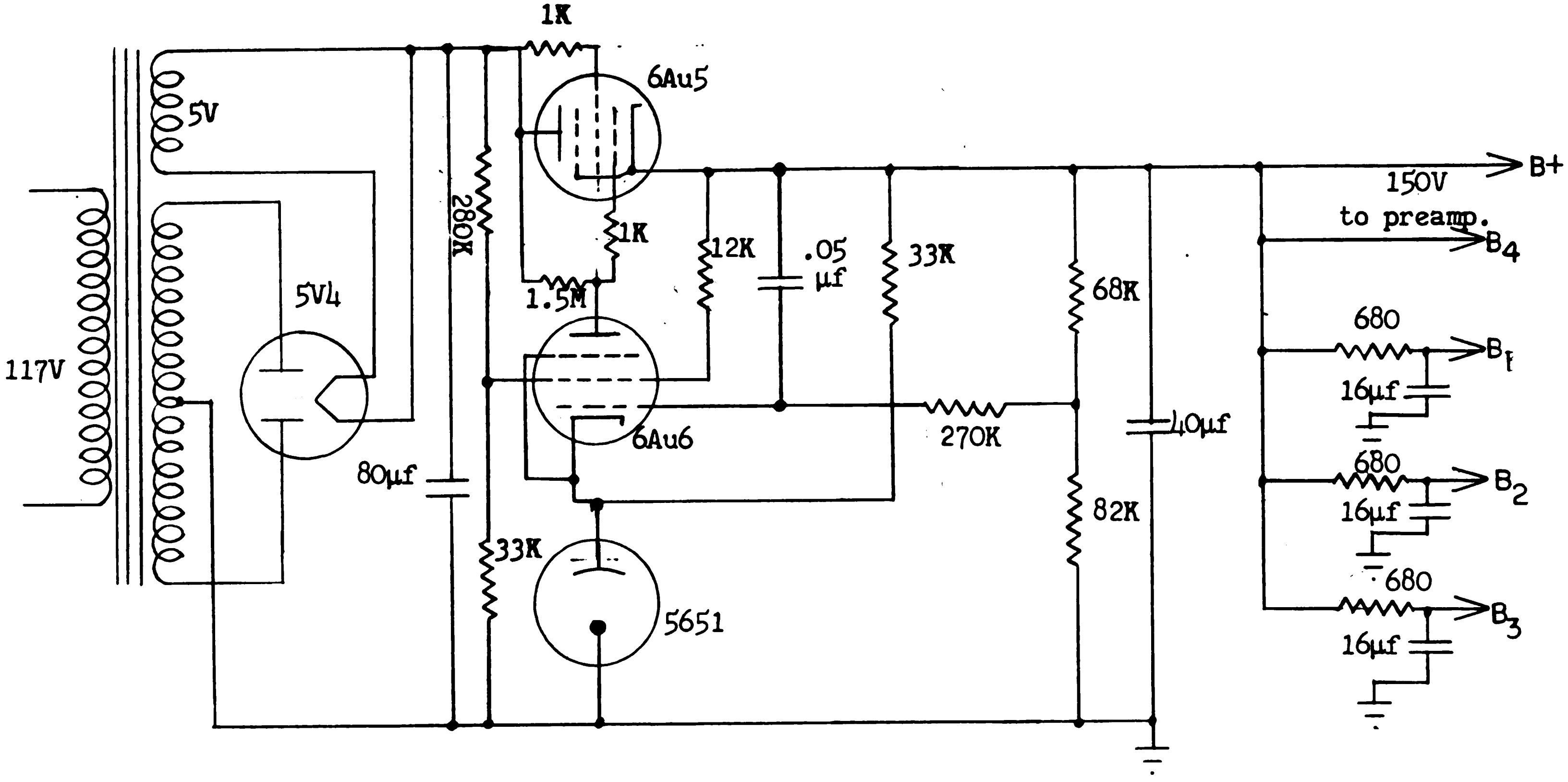


Figure 10. Circuit of the power supply for the preamplifier and the phase sensitive detector.

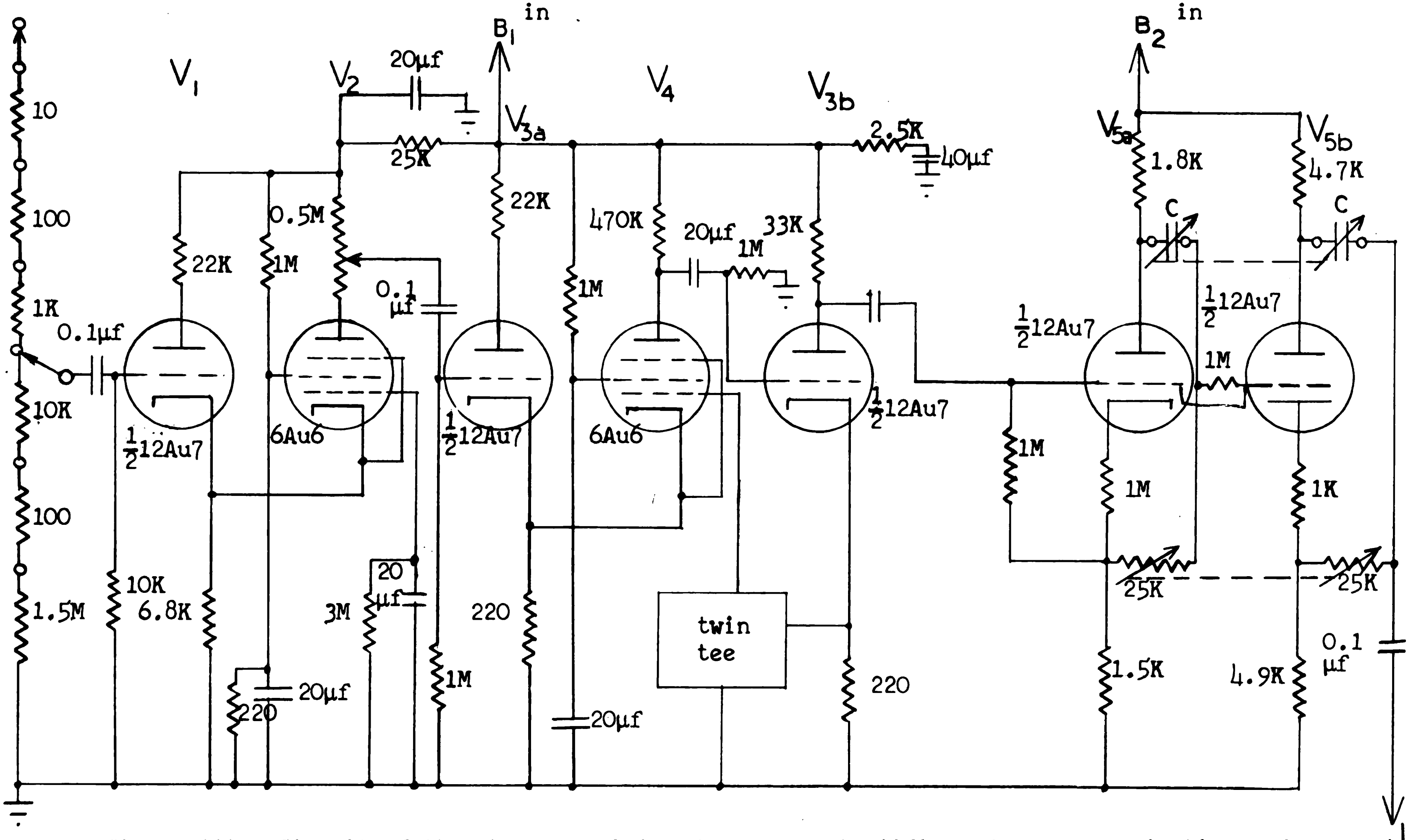


Figure 11A. Circuit of the phase-sensitive detector. Amplifier, frequency selection and phase shift sections.

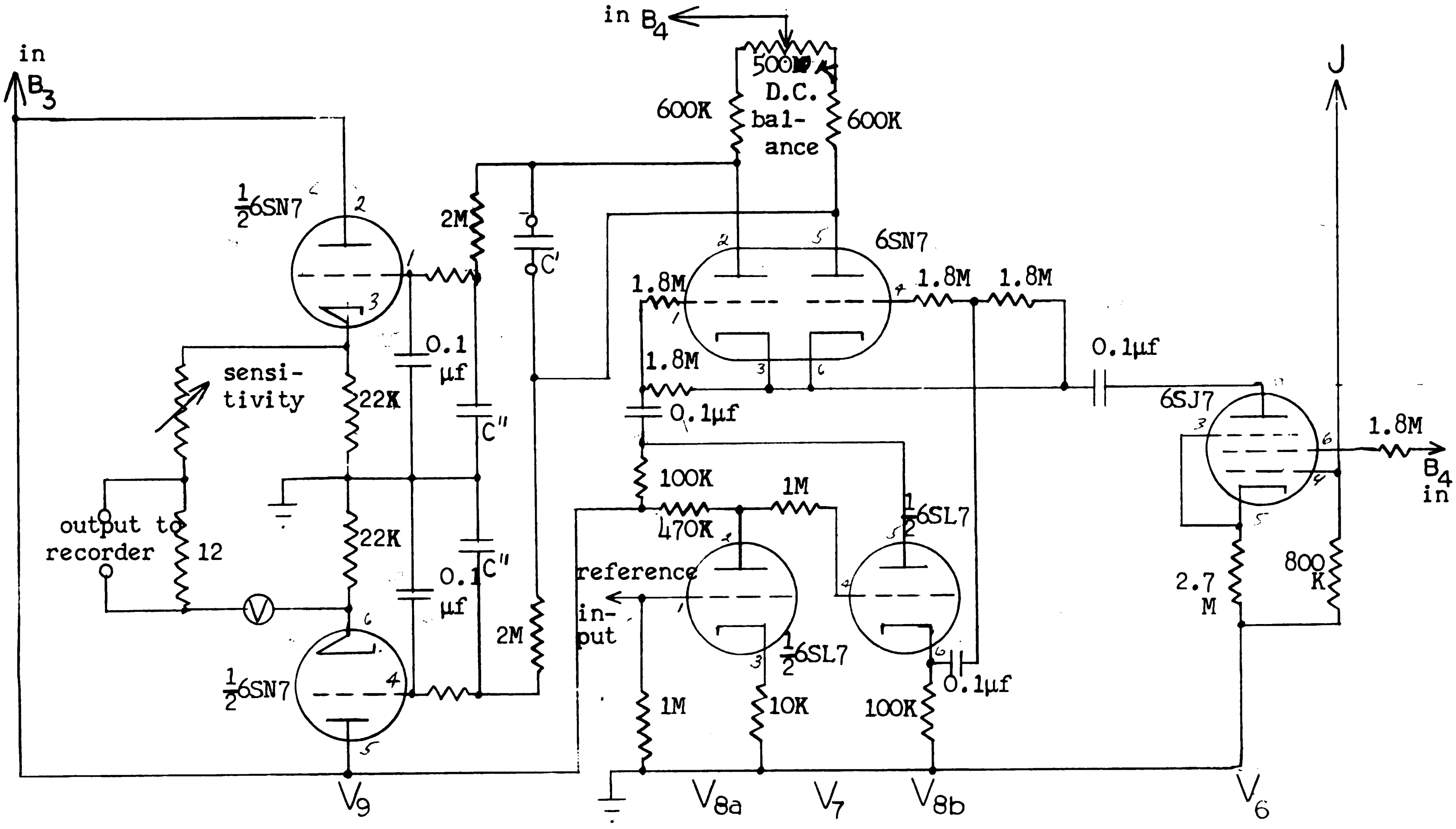


Figure 11B. Circuit of the phase-sensitive detector. Phase sensitive section.

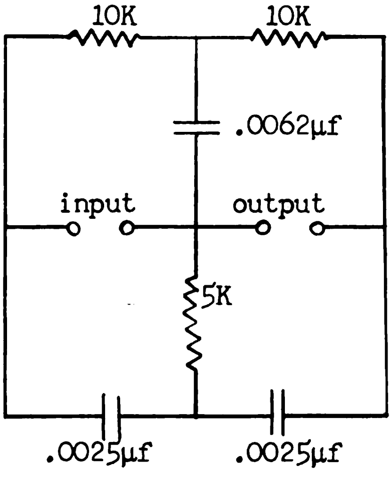
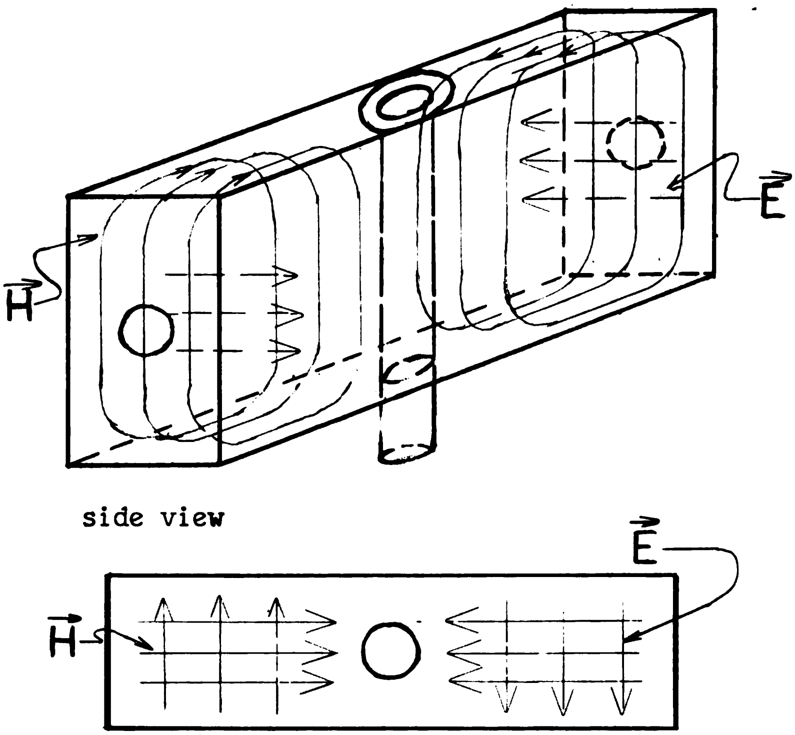


Figure 12. Circuit of the twin tee filter in the phase-sensitive detector.



top view

Figure 13. Sample cavity and fittings, indicating the standing wave pattern for oscillation in the TE_{102} mode.

Sample Cavity

The sample cavity is a rectangular section of waveguide in which the microwave radiation is reflected back and fourth many times before emerging, and which is placed between the centers of the magnet pole caps. The cavity is constructed so that it will resonate in the TE_{102} mode. (see Figure 13). Use of this mode of oscillation allows the sample to be inserted into a region of maximum magnetic field intensity and minimum electric field intensity. Since it is the magnetic component of the radiation which causes the magnetic dipole transition observable in E.S.R., such placement is desirable. When the sample is in the position indicated in the figure, the polarization of the radio frequency field is perpendicular to the static external magnetic field.

The Q, or figure of quality, of a cavity resonator has the same significance as for any resonant circuit. For convenience, the Q of a cavity is often based on the definition:[83]

$$Q = 2\pi \frac{\text{energy stored}}{\text{energy lost per cycle}}$$

The basic definition of Q is that in the measurement of the response of the cavity as a function of frequency, when the response has dropped to 70.7% of the response at resonance, the separation from resonant frequency (measured in cps) is the resonant frequency divided by 2Q.

$$|\nu_0 - \nu| = \frac{\nu_0}{2Q} \tag{26}$$

or

$$Q = \frac{\nu_0}{\Delta\nu} \tag{27}$$

where ν_0 is the frequency at resonance

ν is the frequency at 70.7% response

$\Delta\nu$ is the change of frequency between points at which response is 70.0% of that at ν_0

Equation (27) was used to measure Q.

Several cavities are available for this spectrometer. All cavities were made from sections of waveguide out to the proper length, with end plates soldered to them. These end plates each have a circular iris in the exact center. A 5/16 inch hole is drilled in the center of the top of the cavity for sample insertion, and a matching hole is drilled in the center of the bottom.

The waveguide originally was silver-plated on the interior, but much of this was stripped in soldering. Therefore, after construction, the cavity interior was replated. Areas to be plated were first sanded, then vapor-degreased using trichloroethylene, and further cleaned using the copper bright dip. A blue dip was used to give a mercury immersion plate for a basic coat. To get a white silver plate of satisfactory coverage and adhesion, a silver strike bath was used with 99.9% silver anodes, applying a strike at high current density and then a plate at lower current density in the same bath.

The best cavity available was 1.701 inches in length with irises of 3/16 i.d. This cavity gave a Q of 3477 when empty, resonating at 9389.0 mc. With a sample of DPPH in a glass tube inserted in this cavity the Q was found to be 2228, with resonance at 9359 mc.

The cavity is fitted with a sample tube. This is merely a two-inch cylinder fashioned from Kel-F, with an internal diameter of 1/4 inch, and an external diameter of 5/16 inch. There is a lip on the top 1/8 inch in thickness and 1/2 inch in diameter, which prevents the tube

from being pushed down and out of the cavity. This sample tube eliminates the possibility of any sample being lost into the interior of the cavity.

A small indentation and hole were made into one side of this tube, just below the cavity. The indentation serves to prevent samples not supported from above from slipping down through the cavity. A copper-constantan thermocouple was inserted through the hole to measure cavity temperature.

Frequently it is necessary to observe spectra at low temperatures. This is particularly true in the case of free radicals formed through irradiation, such as are studied here. In many cases these free radicals are destroyed or changed at room temperature. For spectra taken at low temperatures, a flow of cold air was used to refrigerate the cavity. The laboratory compressed air supply was first filtered through glass wool, and then run through two traps. The first trap was immersed in ice water, the second in liquid air. Thus all particles, and most of the moisture was removed from the air. The air stream was then passed through a coil of copper tubing immersed in a Dewar flask of liquid air located directly below the cavity, to cool the air. The stream of cold air then flows directly into the cavity, the copper tubing being connected to the bottom of the sample tube. Adquate room is left in the sample tube, so that the air flow can readily pass around any sample, and out of the top, escaping into the atmosphere.

The temperature of the cavity is adjusted by varying the rate of flow of air. A small galvanometer which had been shunted to give a greater sensitivity, was used to read the cavity temperature as indicated by the thermocouple. In order to calibrate the reading of this galvanometer in terms of true cavity temperature, simultaneous readings were taken on it, and on a highly accurate galvanometer, connected to a second copper-constantan thermocouple which was inserted into the cavity from the top, to the same depth as a normal sample. The lowest temperature registered using this method of cooling was -162°C. Using this method temperatures are easily read to within 1°.

The Commercial Spectrometer

The commercial spectrometer used after June, 1962, was made up of the following units. The magnetic field is produced by a rotating 12-inch Varian Magnet, powered by a Varian Regulated Magnet Power Supply. Control of the magnetic field is given by a Varian E.P.R. Control Unit Model V4500-10A with a Varian Precision Field-Scanning Unit Model V4280A. For the power and control of wobbling coils in this spectrometer, a Varian 100 kc/sec Field Modulation and Control Unit Model V4560 has been added.

Measurement of the magnetic field is accomplished in the same manner as described above in the other spectrometer. The same radio-frequency oscillator and probe are used. For the determination of the radio-frequency a Hewlett-Packard Electronic Counter Model 524C is used. This counter has an accuracy of ± 20 cps.

The microwave system of the commercial spectrometer is as follows. A Varian reflex klystron V153C is powered by a Varian Klystron Power Supply model V4500-20. The klystron is combined with a Varian X-band superhetrodyne adaptor and a Varian X-band microwave bridge. In this spectrometer a magic tee is used in the waveguide. On one leg of this tee is a Varian low temperature reflection cavity. On a second leg is the same wavemeter as previously described with a 408B crystal diode detector and a crystal current meter, used in conjuction with the wavemeter for the determination of the klystron frequency. On the third leg of the tee is the detector crystal diode, MA423.

The detected signal from the crystal diode is fed into a Varian Output Control Unit model V4270A, and recorded on a Varian G-10 Recorder.

The temperature of the cavity of this spectrometer is controlled by a Varian E.P.R. Heat Control Unit. In order to prevent the condensation of water in the system, both the waveguide and the cavity itself are swept by a stream of dry nitrogen. The temperature of the cavity is read by the use of a copper-constantan thermocouple connected to a Brown* Potentiometer model 2745.

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*Minneapolis-Honeywell Regulator Co., Brown Instruments Division, Philadelphia, Pennsylvania.

EXPERIMENTAL

Operation of the Spectrometers

The klystron is allowed to warm up for at least two hours before any spectra are taken. This assures complete warm-up of the low voltage power supply, and the establishment of a constant temperature in the oil bath surrounding the klystron tube.

The proper range of magnetic field is selected by the tap used on the dropping coil in the magnet current regulator and control circuit.

The resonant frequency of the cavity varies with temperature and load, thus tuning of the klystron is necessary for each sample at each temperature. With the sample in the cavity, and the temperature set as desired, the repeller voltage is adjusted to give a maximum reading on the crystal current meter. The klystron is mechanically tuned using a knob geared to the mechanical tuner on the klystron tube, again adusting to maximum crystal current. Further fine tuning is accomplished using the tunable crystal mount at the end of the microwave system. The slight retuning necessary during a series of experiments, due to the change in position of the sample or temperature variation, is done by variation of the repeller voltage. The crystal current desired is then set by use of the attenuator.

Along with each spectrum taken, the frequency of the klystron is measured using the wavemeter. When this meter is set on the frequency of the microwaves in the wave guide, a sharp decrease in crystal current is observed, since the microwaves are passed into the coupler, through the wave meter, and are absorbed.

The wobbling coils are turned on, and the current is set between 1/4 and 1 ampere. The line height of the recorded spectrum varies directly with this current, making a high value desirable. However, when phase sensitive detection and pen recording are used, a field modulation sweep greater than one tenth of the absorption line width results in distortion of the line shape.[10] Selection of the current used must be based on these two considerations.

Starting well beyond the region of absorption of the sample, the magnetic field is slowly swept by rotating the Helipot potentiometer in the magnet current control unit, driven by a reversible motor. The resulting field sweep is nearly, but not quite, linear with time.

The determination of the magnetic field strength is accomplished as follows. A series of readings on the frequency meter corresponding to known harmonics of frequencies which give a proton resonance at 50 gauss intervals in the magnetic field region of interest was determined. The frequency meter is set to a reading corresponding to a field value just within the chosen sweep range of the magnet. The marginal oscillator is set to the corresponding frequency by beating the two signals together and adjusting to the null point as observed aurally with a headset. The output of the marginal oscillator is then observed on the oscilliscope. During the sweep of the field, at the point of proton resonance, a positive-going pulse is observed on the oscilliscope screen. At this point a mark is made by grounding the recorder instantaneously with a key. This makes a line on the recorded spectrum, and the recorder pen returns immediately to the recording of the spectrum, with very little resultant distortion to the spectrum.

The operation of the commercial spectrometer is similar, but more automatic. Rough tuning of the klystron is accomplished as above using the crystal current meter. Further refinement in the tuning to the cavity frequency is made by putting a small 40 cps signal on the klystron repeller and observing the resultant signal on the crystal using a Hewlett Packard Oscilliscope Unit model 120AR. Fine tuning then consists of centering the cavity resonance in the node of this signal.

The sweep of the magnetic field is set automatically on this spectrometer, and was assumed linear with time. Therefore, only two field markers were placed on these spectra, at the beginning and end of each spectrum. The frequency for which the marginal oscillator is set to give the proton resonance is read directly from a Hewlett Packard Electronic Counter.

Sample Preparation

Most of the samples were reagent grade Eastman Chemicals but several were prepared in these laboratories for NMR studies. The purification and properties of several have been described.[84]

Cylindrical containers small enough to slip easily into the cavity tube were used to hold liquid and powder samples. These containers were made by heat sealing trithene film to form a tube and closing both ends by heat sealing. Cotton thread was tied through a hole in the sealed area at one end for ease of handling the sample. The samples run by K. R. Way were placed in Kimax capillary tubing, (1.5 - 2.0 mm in diameter, 50 mm. in length) sealed at both ends, with a thread attached to the tube with Goodyear Pliobond.

All samples were irradiated with 1 MEV electrons from the General Electric* Resonant Transformer located in the Agricultural Engineering Department of Michigan State University, operating at maximum current (1 ma). Irradiation time was ten minutes, the samples being turned over after half of the irradiation time.

All samples were irradiated at a low temperature using the following method. A Thermos bottle was filled to within a few inches of the top with liquid air on which was placed a float made of cork or of foam glass, covered with aluminum foil. The volume of the float was such that the upper surface was just above the liquid air surface. Grooves were molded in the top of the float which were just at the liquid surface, allowing some liquid to flow into the grooves. Sample tubes were laid in these grooves during irradiation. The temperature at the top of the samples in such a position was found to be -173°C.

After completion of irradiation, the attached thread was used to slip each sample off the float into the liquid air, and to anchor the sample to the Thermos** flask. With the float removed, the Thermos was kept filled with liquid air for storage of the samples until spectra were taken. In most cases storage time was only a matter of a few hours. The cavity was always cooled to operating temperature before insertion of the sample, and it is not felt that the time involved in rapidly transferring the sample from the storage Thermos to the cavity, using the thread as a handle, allowed any significant warming. The cavity temperature of the M.S.U.-built spectrometer was about 138°K, that of the Varian spectrometer varied from 110° to 123°K.

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*General Electric Co., Schnectady, New York.

**American Thermos Products Co., Norwich, Connecticut.

The sample cylinders were of such a diameter that the only adjustment necessary within the cavity was for vertical placement and this could be done easily with the attached thread.

All materials used as sample containers, which were irradiated and present during the recording of spectra, were checked and those chosen which gave no interferring spectra.

The Matching of Spectra

The lines observed in E.S.R. spectra approach either a Gaussian or Lorentzian shape depending upon the broadening mechanism present. Dipole-dipole interactions are the chief source of Lorentzian broadening, and with the low radical concentrations present in irradiated samples, these may be neglected.[57] The lines observed are thus expected to be Gaussian in shape, and this is usually found to be the case in such studies.

The theoretical curves to which the experimental spectra are matched are Gaussian derivative curves obtained from MISTIC, the Michigan State University computer, using a program devised by Dr. J. Roger Faber. The input data consist of values for line width, spacing between adjacent peaks, and the center point of the spectrum, combined with specifications for the number of lines, the equivalence of spacing between them, and the relative intensities for each. To obtain the theoretical curves used here series of three, five and seven equally spaced lines of intensities corresponding to the binomial coefficients were calculated. Variations were made in the data input for line width between points of inflection and peak spacing. Therefore, the MISTIC curve, or theoretical curve is most easily specified by stating the ratio of the peak separation to the line width. Due to the overlapping of the lines in the spectra, the intensities and the peak separations in the theoretical curves do not match those of the input data in appearance. In all cases in which relative intensity is mentioned, it refers to the value for the original theoretical spectrum, not the apparent one.

Selection of the MISTIC spectrum to be used as the theoretical curve to match the experimental curve was done by matching the values at the points of inflection. The two variables are the multiplier of the experimental values, and the theoretical curve used. A combination of these two was sought which gives a minimum value for the sum of the squares of the differences between experimental and theoretical values. The one exception to this procedure was in the matching of the spectrum shown in Figure 30b, for which a five line spectrum and a seven line spectrum fit equally well. Here the choice was made on the basis of matching the peak separations.

To determine the numerical values for peak separation and line width of those spectra which were measured, the spacing between adjacent points of inflection on the experimental spectrum was compared to the spacing between similar inflection points as they appeared on the previously selected theoretical curve. A factor was determined such that the product of the factor and the experimental spacing best matched the apparent theoretical spacing. The criterion used for selection was again a minimal value for the sum of the squares of the differences. This factor and the proton frequency markers were then used to determine the values in gauss corresponding to the input data for line width and peak separation of the theoretical spectrum.

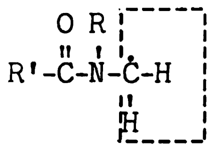
Experimental Results

N-methylamides

Eight amides having methyl substituents on the nitrogen were irradiated and the spectra were taken. These spectra are shown in Figures 14-21. Table IV lists the parameters determined for the spectra.

All compounds studied of the this type give a three-line spectrum with line intensity ratios of 1:2:1. In light of the previous discussion of hyperfine splitting patterns, the hyperfine spectra observed must come from two hydrogen nuclei interacting equivalently with the unpaired electron spin.

From the diversity of the compounds used, it is apparent that the radiation damage and the resulting odd electron spin must occur in the methyl group substituted on the nitrogen of the amides. The radical proposed to account for these spectra is;



$$R'-\overset{O}{\overset{\|}{C}}-\overset{R}{\overset{|}{N}}-\underset{\underset{H}{|}}{\dot{C}}-H$$

where R is either H or CH_3

and R' is CH_3, CH_2CH_3, $(CH_2)_2CH_3$, $CH(CH_3)_2$, $CH{=}CH_2$, or CH_2Cl

The atoms enclosed by the dotted lines are those interacting with the unpaired electron.

Line widths and coupling constants listed in Tables IV and V have an accuracy of ± 1 gauss or better.

—— experimental

⊙ ⊙ ⊙ calculated

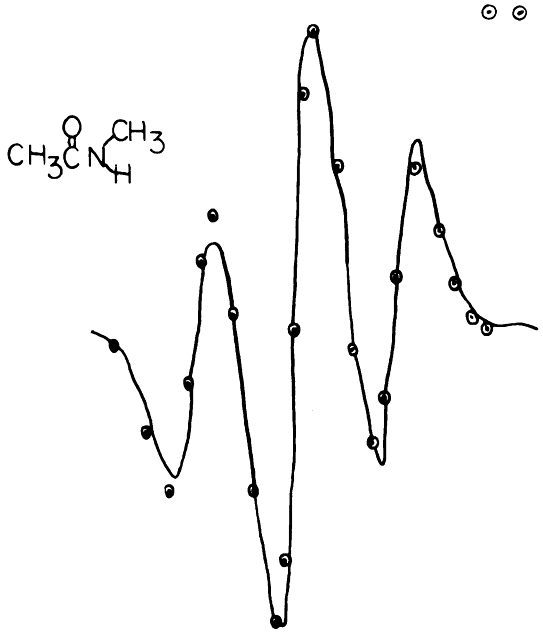


Figure 14. Experimental spectrum of N-methylacetamide and the matching theoretical spectrum.

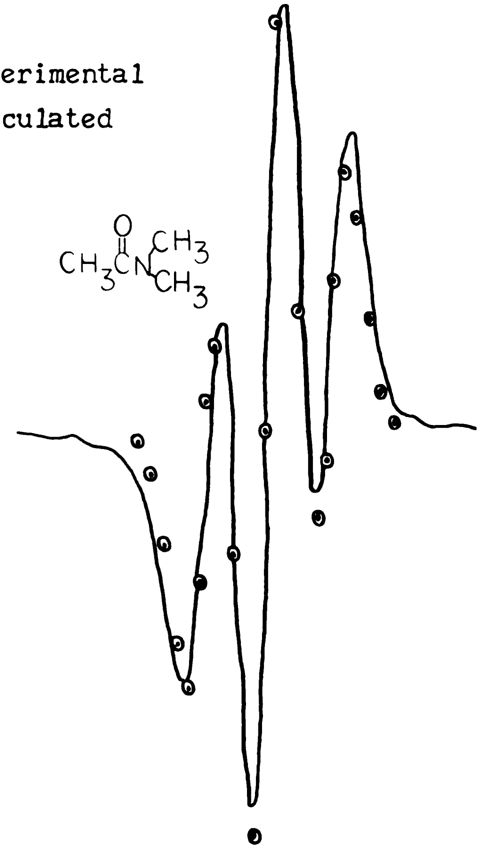


Figure 15. Experimental spectrum of N,N-dimethylacetamide and the matching theoretical spectrum.

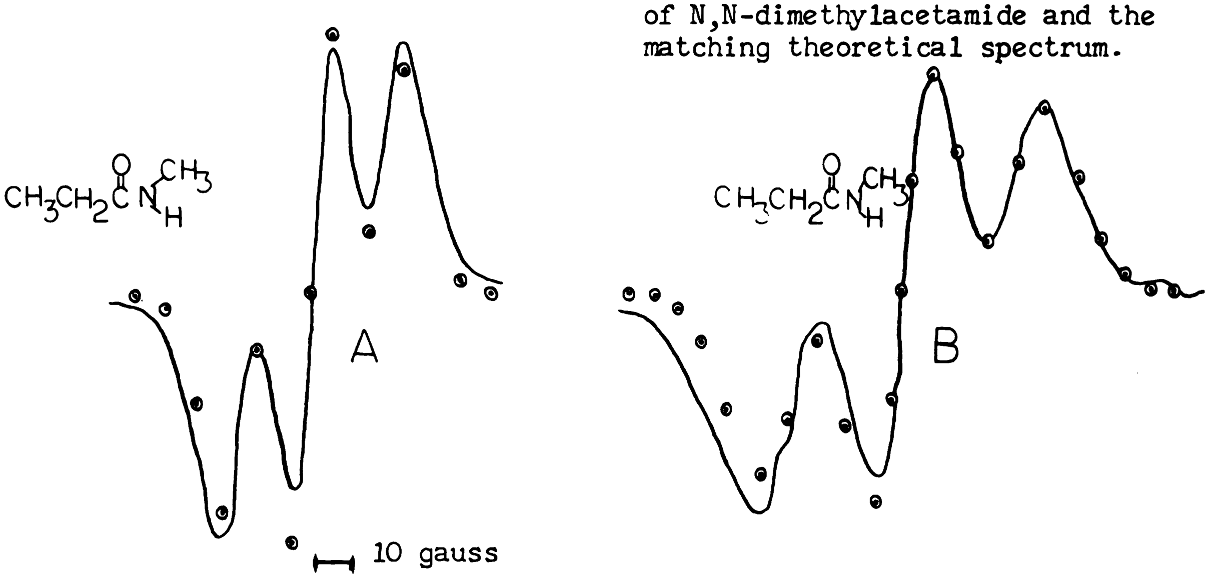


Figure 16. Experimental spectra of N-methylpropionamide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

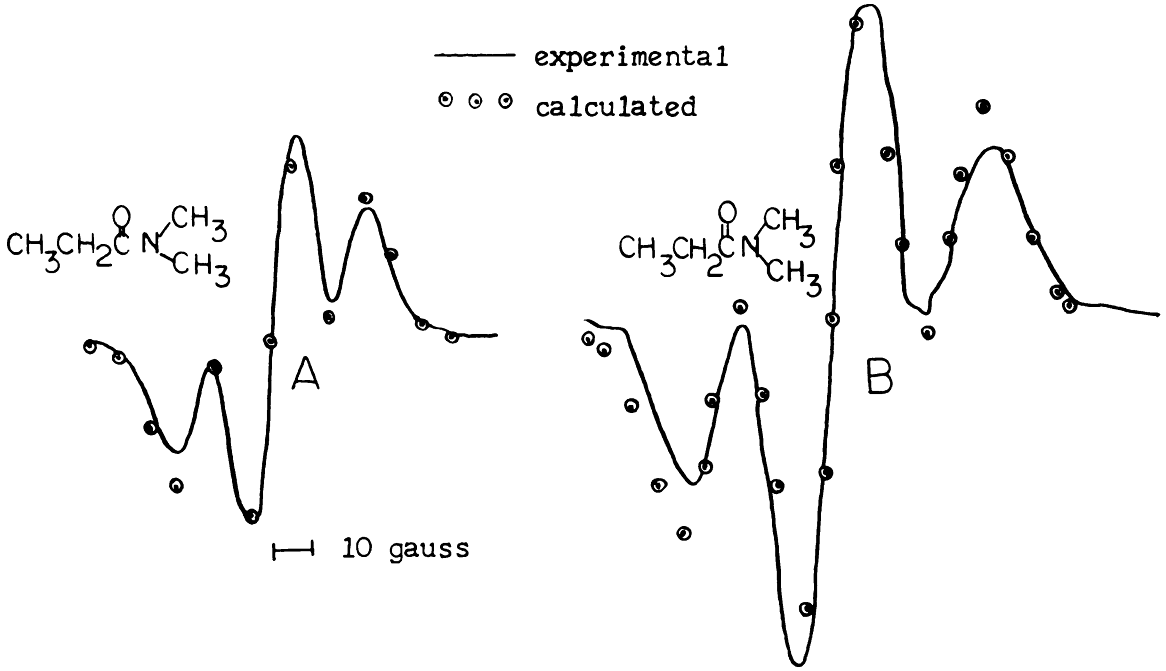


Figure 17. Experimental spectra of N,N-dimethylpropionamide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

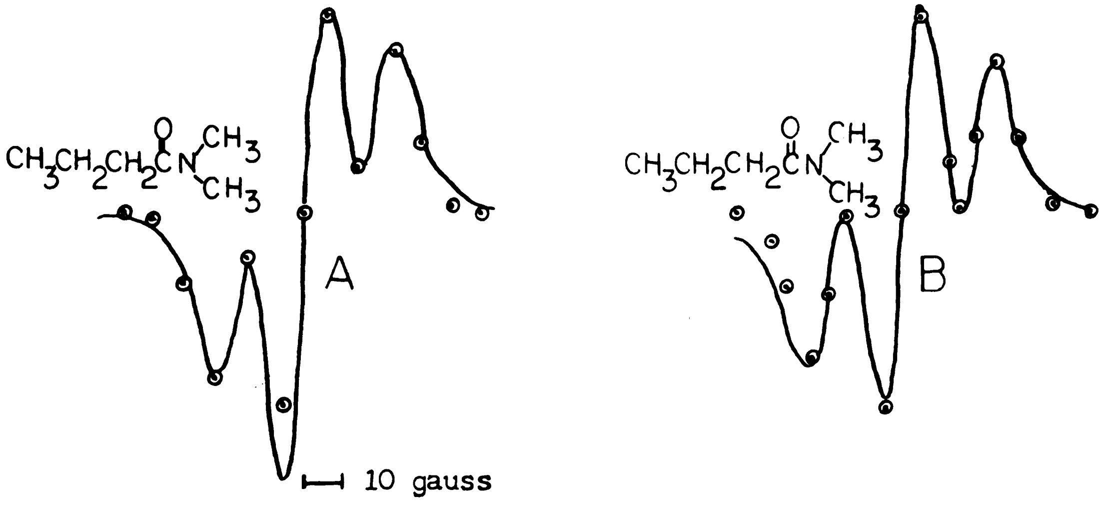


Figure 18. Experimental spectra of N,N-dimethylbutyramide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

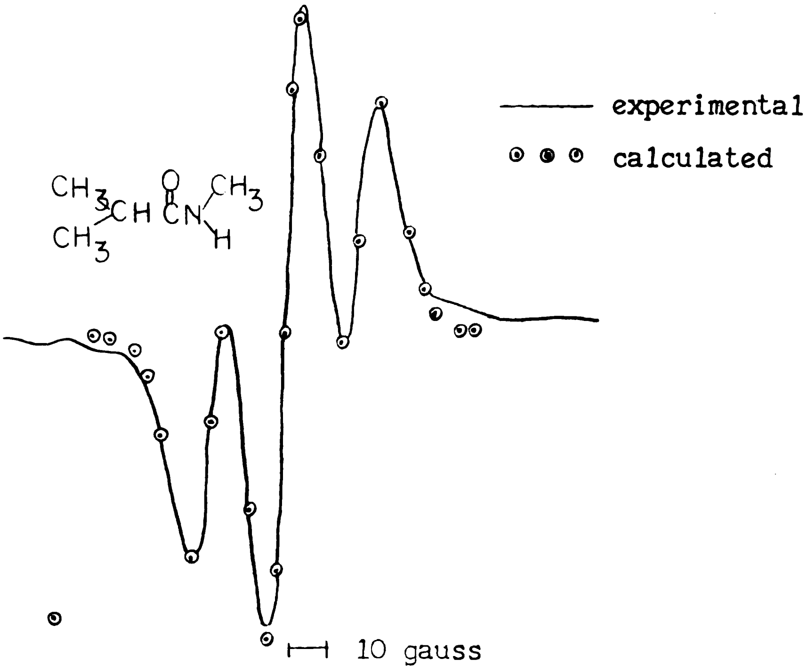
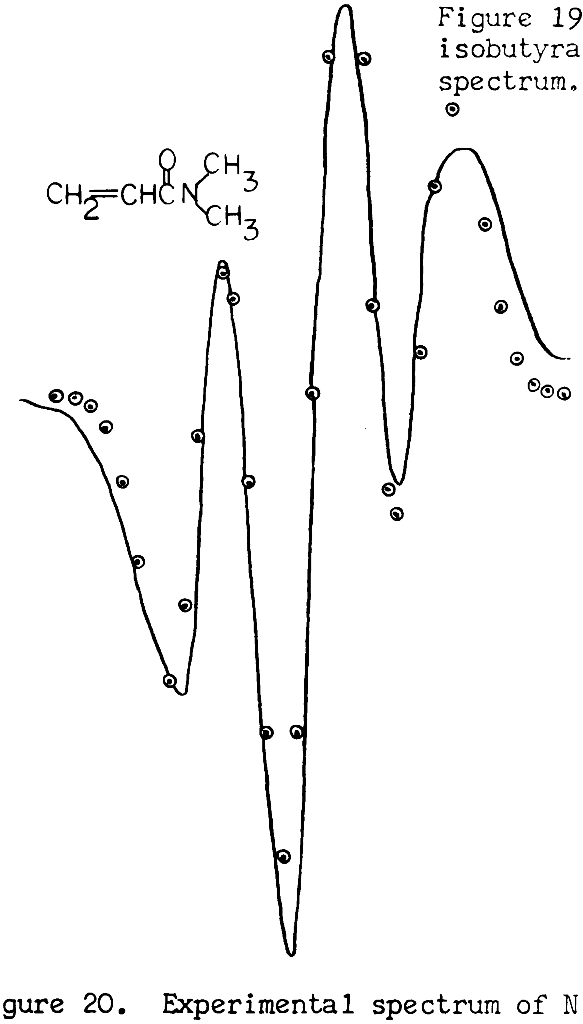


Figure 19. Experimental spectrum of N-methylisobutyramide and the matching theoretical spectrum.



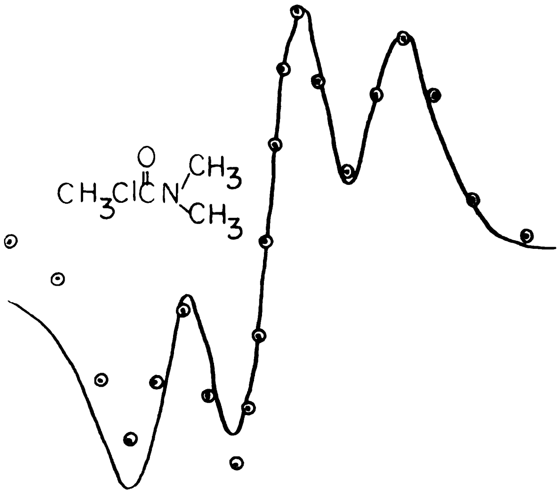


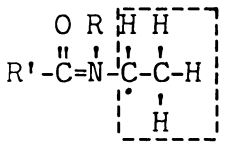
Figure 21. Experimental spectrum of N,N-dimethylchloroacetamide and the matching theoretical spectrum.

Figure 20. Experimental spectrum of N,N,-dimethylacrylamide and the matching theoretical spectrum.

N-ethylamides

Six amides having one or two ethyl groups substituted on the nitrogen were studied. The spectra for these amides are shown in Figures 22-29, and the parameters determined for them are listed in Table IV.

This type of compound gives a five-line spectrum, the intensity ratios of the lines being 1:4:6:4:1. Of the nuclei present possessing spin, only a combination of four protons interacting equivalently with the electron spin can produce the observed pattern. Again the variety of amides used leads to the conclusion that the unpaired electron spin is located in the group bonded to the nitrogen. The radical proposed to give this result is:



$$R'\text{-}\overset{\overset{O}{\|}}{C}=\overset{\overset{R}{|}}{N}\text{-}\underset{\cdot}{\overset{\overset{H}{|}}{C}}\text{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\text{-}H$$

where R is either H or CH_2CH_3

and R' is H, CH_3, CH_2CH_3, $(CH_2)_2CH_3$, $CH(CH_3)_2$, $CH{=}CH_2$, or CH_2Cl

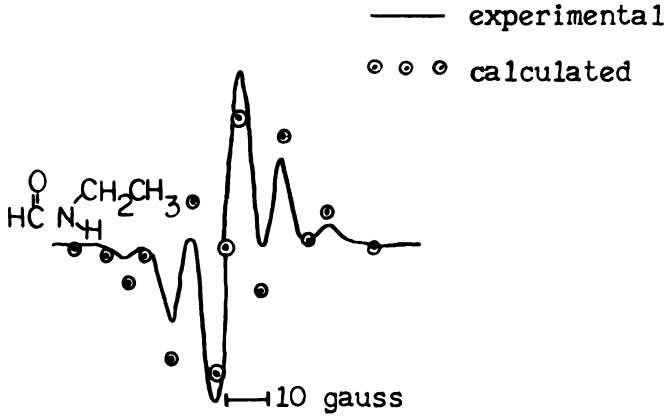


Figure 22. Experimental spectrum of N-ethylformamide and the matching theoretical spectrum.

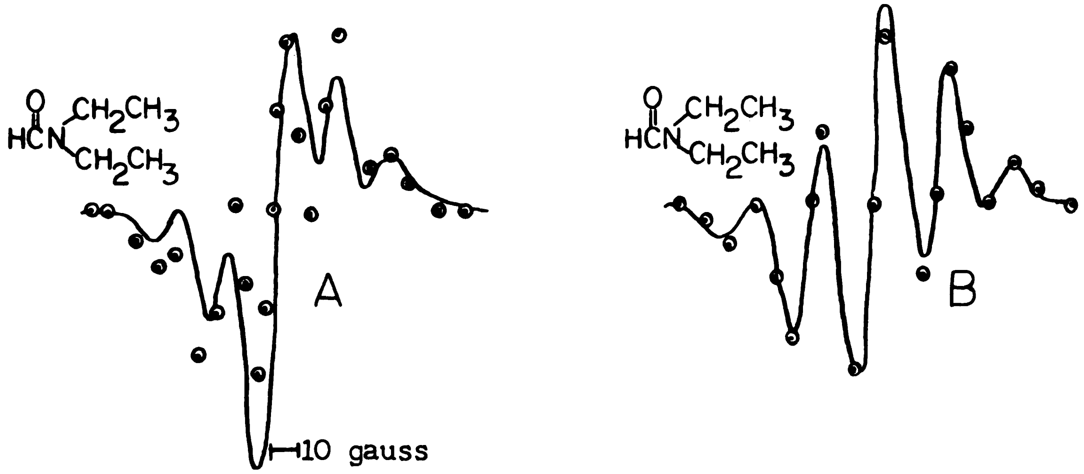


Figure 23. Experimental spectra of N,N-diethylformamide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

—— experimental

⊙ ⊙ ⊙ calculated

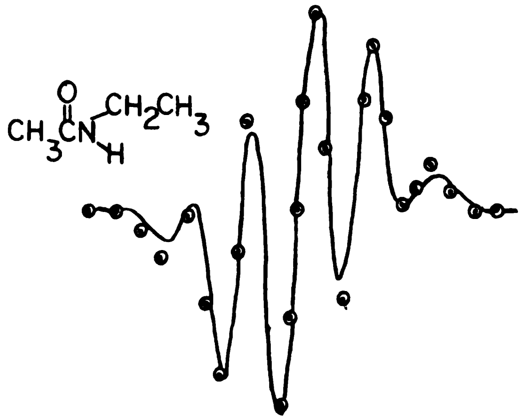


Figure 24. Experimental spectrum of N-ethylacetamide and the matching theoretical spectrum.

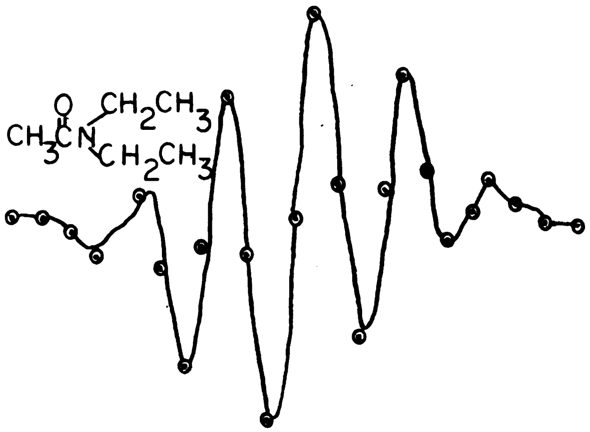


Figure 25. Experimental spectrum of N,N-diethylacetamide and the matching theoretical spectrum.

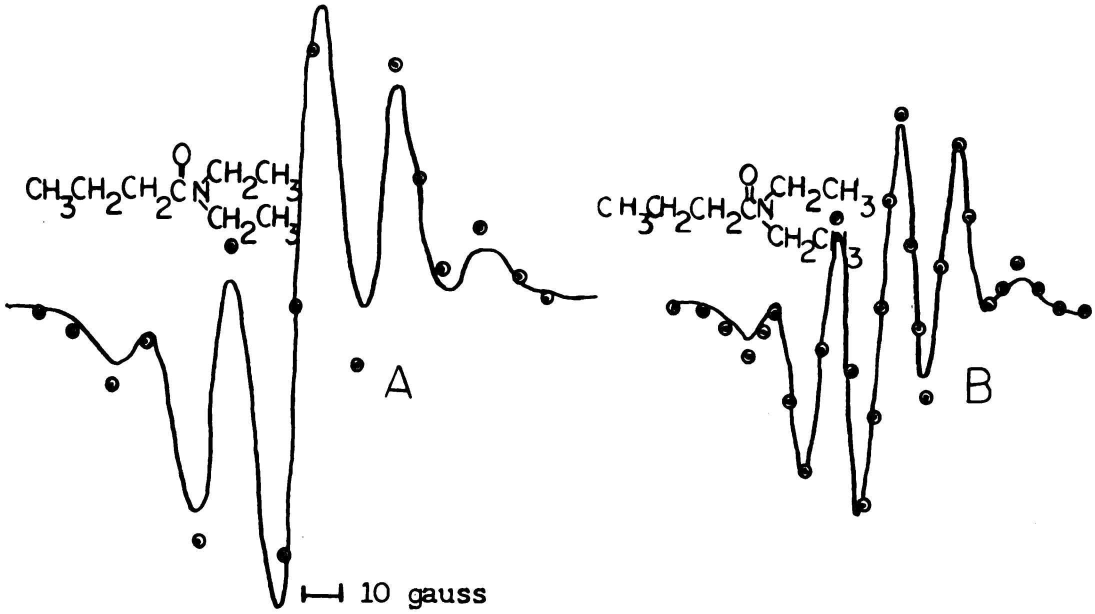


Figure 26. Experimental spectra of N,N-diethyl-n-butyramide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

——— experimental

● ● ● calculated

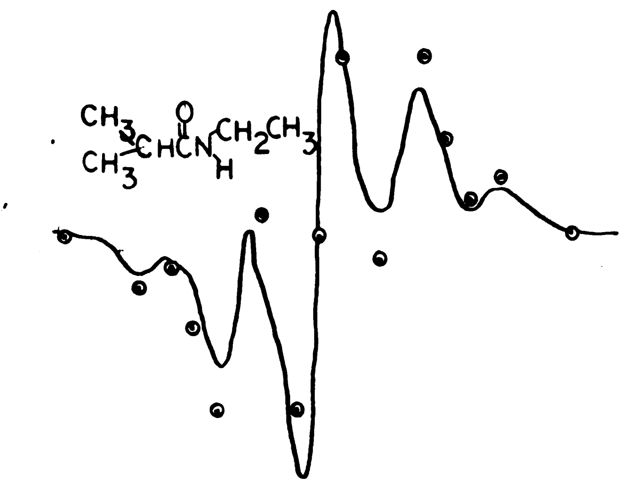


Figure 27. Experimental spectrum of N-ethylisobutyramide and the matching theoretical spectrum.

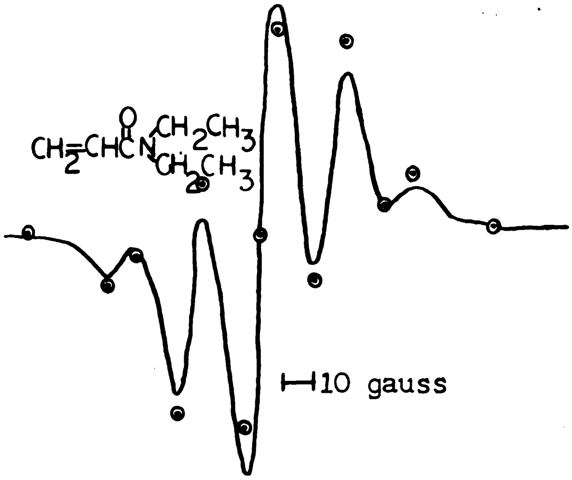


Figure 28. Experimental spectrum of N,N-diethylacrylamide and the matching theoretical spectrum

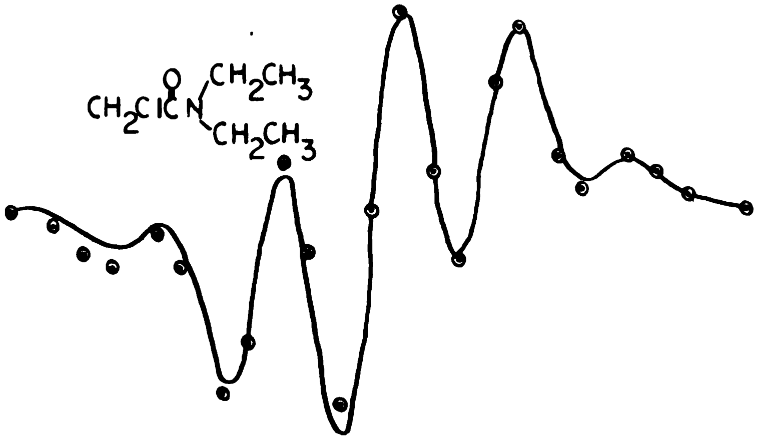
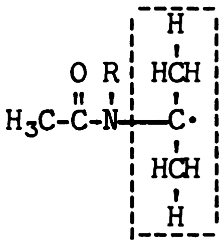


Figure 29. Experimental spectrum of N,N-diethylchloroacetamide and the matching theoretical spectrum.

N-propylamides

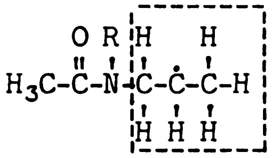
Spectra were also taken of three amides having propyl groups substituted on the nitrogen. Both normal propyl and isopropyl substitutions were used. These spectra are shown in Figures 30-32, and the related parameters are given in Table IV.

These amides all given spectra of seven lines, with intensity ratios 1:6:15:20:15:6:1. Such a pattern is possible here only from the equivalent interaction of six hydrogen nuclei. Since all of these compounds are substituted acetamides, the requisite number of hydrogen nuclei is present only in the propyl groups on the nitrogen, leading to the conclusion that this is the location in which radiation damage occurs. The proposed radicals are;



$$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-\overset{\overset{\overset{H}{|}}{HCH}}{\underset{\underset{\underset{H}{|}}{HCH}}{\overset{|}{\underset{|}{C}}}}\cdot$$

and



$$H_3C-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\cdot}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

where R is H or C_3H_7.

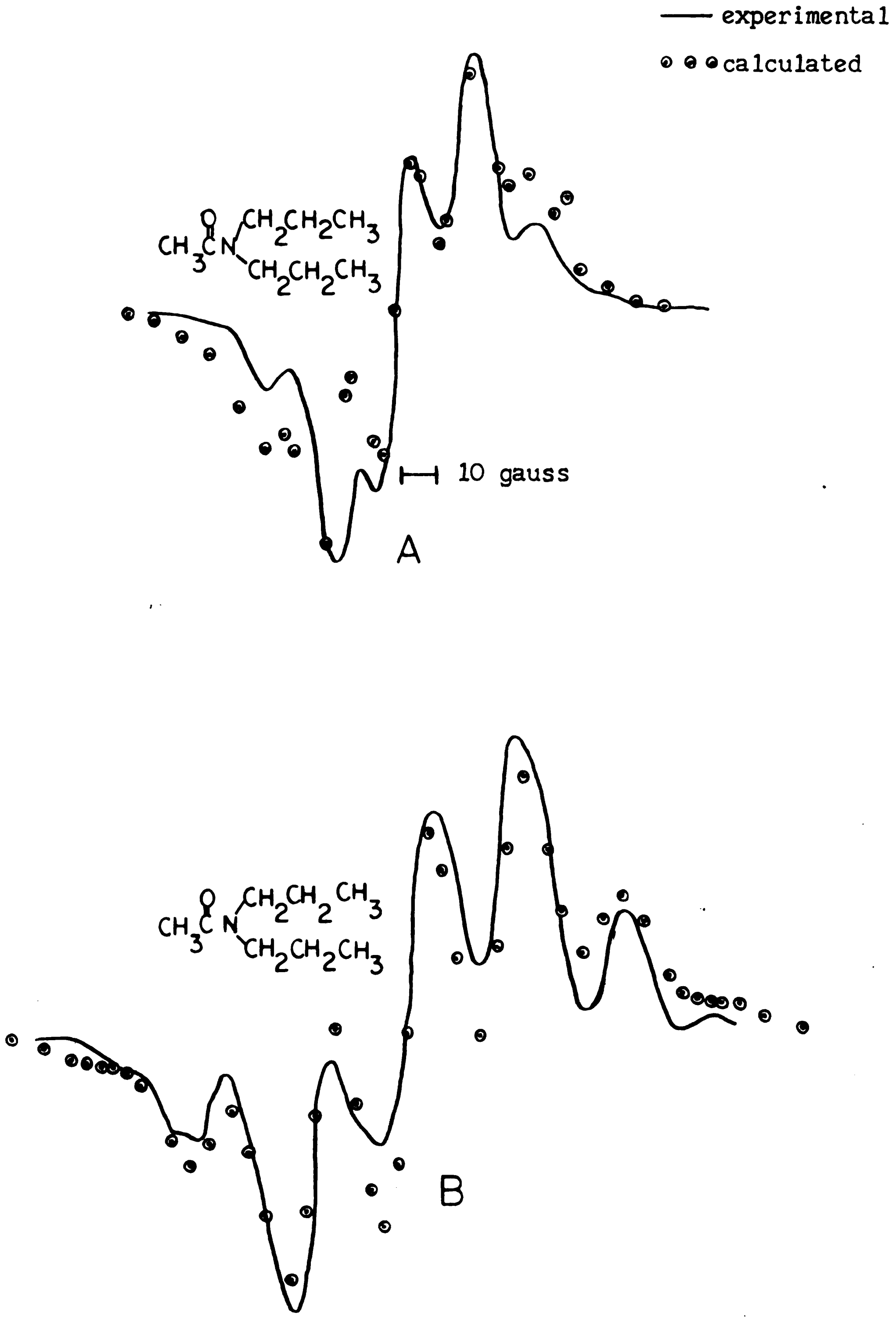


Figure 30. Experimental spectra of N, N-di-n-propylacetamide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

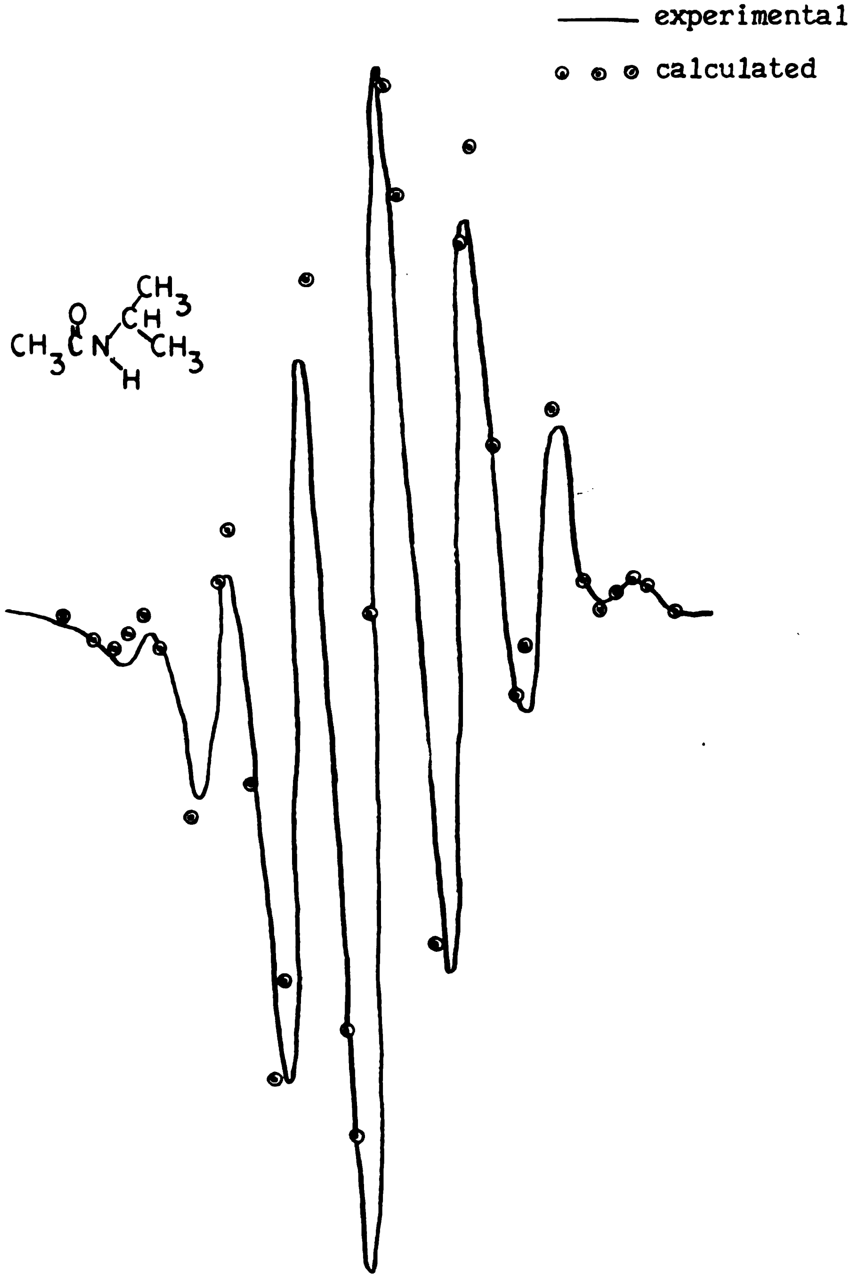


Figure 31. Experimental spectrum of N-isopropylacetamide and the matching theoretical spectrum.

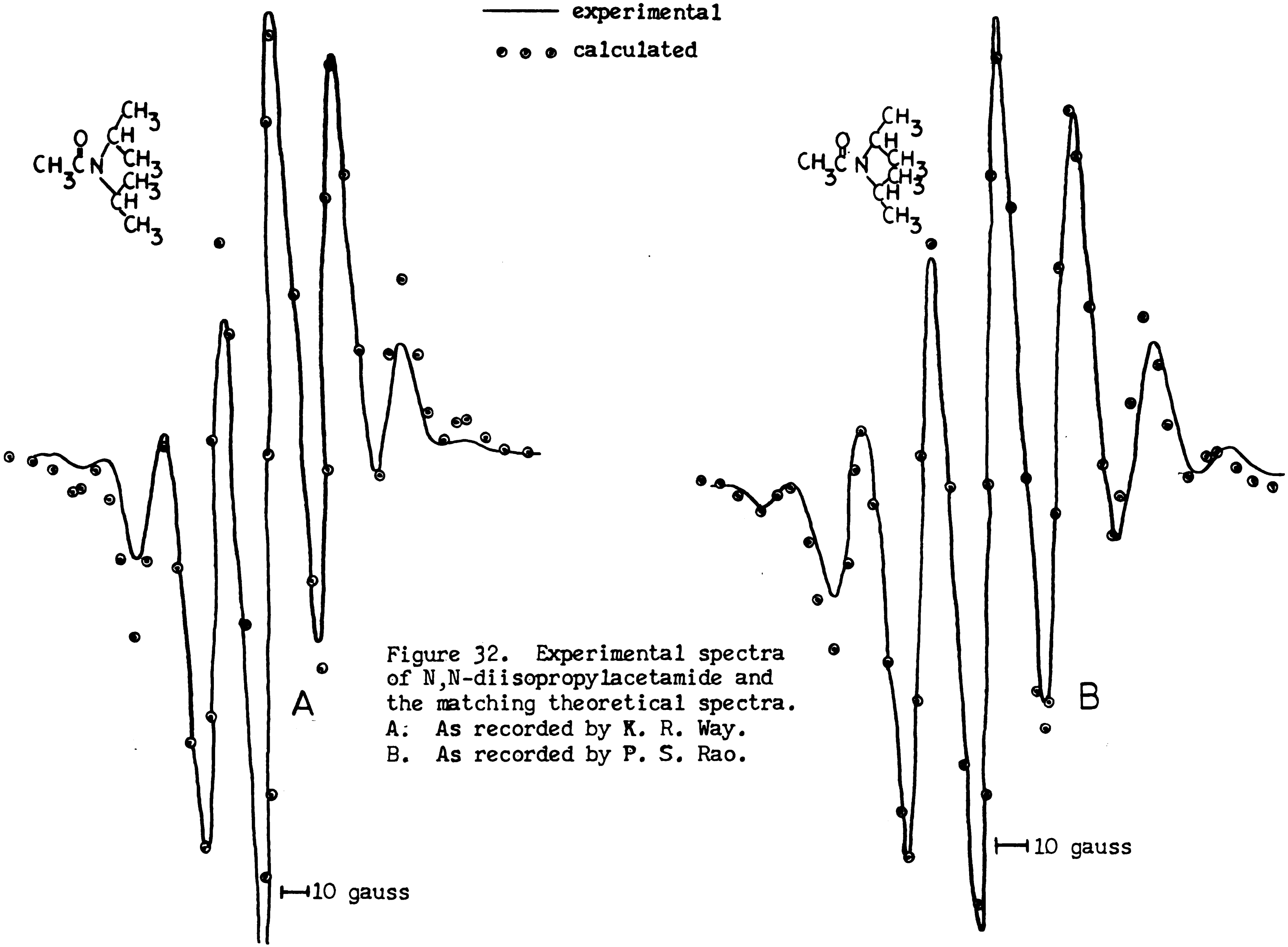


Figure 32. Experimental spectra of N,N-diisopropylacetamide and the matching theoretical spectra.
A: As recorded by K. R. Way.
B. As recorded by P. S. Rao.

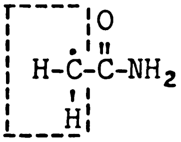
Table IV. Parameters of the E.S.R. spectra of irradiated N-substituted amides.

Compound Irradiated	No. of lines	Line width (gauss)	a peak spacing (gauss)	ratio a/lw	rec'd by	shown in figure
N-Methylacetamide	3	---	---	1.72	Rao	14
N,N-Dimethylacetamide	3	---	---	1.475	Rao	15
N-Methylpropionamide	3	14.5	17.1	1.18	Way	16A
N-Methylpropionamide	3	---	---	1.20	Rao	16B
N,N-Dimethylpropionamide	3	14.2	17.5	1.24	Way	17A
N,N-Dimethylpropionamide	3	---	---	1.34	Rao	17B
N,N-Dimethylbutyramide	3	14.0	16.8	1.20	Way	18A
N,N-Dimethylbutyramide	3	---	---	1.30	Rao	18B
N-Methylisobutyramide	3	14.7	19.6	1.33	Way	19
N,N-Dimethylacrylamide	3	---	---	1.52	Rao	20
N,N-Dimethylchloroacetamide	3	---	---	1.17	Rao	21
N-Ethylformamide	5	---	---	1.40	Rao	22
N,N-Diethylformamide	5	16.7	20.4	1.225	Way	23A
N,N-Diethylformamide	5	---	---	1.475	Rao	23B
N-Ethylacetamide	5	---	---	1.45	Rao	24
N,N-Diethylacetamide	5	---	---	1.45	Rao	25
N,N-Diethyl-*n*-butyramide	5	15.2	20.1	1.325	Way	26A
N,N-Diethyl-*n*-butyramide	5	---	---	1.45	Rao	26B
N-Ethylisobutyramide	5	---	---	1.27	Rao	27
N,N-Diethylacrylamide	5	15.5	20.6	1.33	Way	28
N,N-Diethylchloroacetamide	5	---	---	1.33	Rao	29
N,N-Di-*n*-propylacetamide	7	17.5	18.4	1.05	Way	30A
N,N-Di-*n*-propylacetamide	7	---	---	1.17	Rao	30B
N-Isopropylacetamide	7	---	---	1.55	Rao	31
N,N-Diisopropylacetamide	7	16.0	22.7	1.42	Way	32A
N,N-Diisopropylacetamide	7	14.7	22.1	1.50	Rao	32B

Amides, Carboxylic Acids and Others

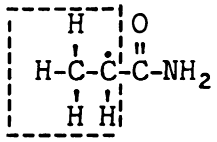
A series of amides not substituted on the nitrogen was also run. The spectra of these amides are shown in Figures 33-41, and the related parameters are given in Table V.

Acetamide gives a three-line spectrum with line intensities in the ratio 1:2:1. As in the above mentioned spectra, this pattern must be due to two proton nuclear spins interacting equivalently with the unpaired electron spin. In this case however, radiation damage must occur in the alkyl part of the molecule bonded to the carbonyl group. The reasonable radical is:



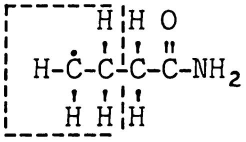
$$H-\underset{H}{\dot{C}}-\overset{O}{\overset{\|}{C}}-NH_2$$

Propionamide gives a five line spectrum with line intensity ratios 1:4:6:4:1. This suggests a similar type of radical with four equivalent hydrogen interactions:



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\dot{C}}-\overset{O}{\overset{\|}{C}}-NH_2$$

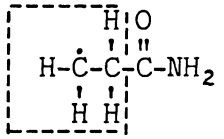
The spectrum of <u>n</u>-butyramide is not that which might be expected from the next amide in the series. The spectral pattern obtained is complex, having nine or perhaps ten lines. Apparently more than one species of radical is present. The dominant lines of the spectrum fall into a pattern of five lines with intensity ratios 1:4:6:4:1. The theoretical points and parameters for these five lines only are shown in Figure 35 and Table V, respectively. The equivalent interaction of four hydrogen nuclei must be used to interpret these results. A possible radical would be:



$$\text{H-}\overset{\bullet}{\underset{\text{H}}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH}_2$$

If this is the radical present it would necessitate the assumption of proton removal from a methyl group which is not usually observed if any other choice is possible.

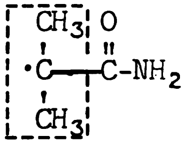
Another possible explanation in this case is the breaking of a C-C bond and the loss of a methyl group, either by the initial radiation or as a secondary reaction. The radical would then be:



$$\text{H-}\overset{\bullet}{\underset{\text{H}}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\text{-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-NH}_2$$

It was not possible to resolve the remaining smaller lines of this spectrum, thus the identity of the other radical species which apparently is present cannot be determined. It can be said, however, that the other lines do not appear to be due to the interaction of one or both of the hydrogen atoms of the carbon next to the carbonyl group interacting as non-equivalent nuclei. Such an interaction would result in the formation of a doublet, or a 1:2:1 triplet from each of the five fominant lines of the spectrum. Neither the intensities nor the placement of the 'extra' lines observed suggest such a splitting. From the results observed for carboxylic acids,[75] radical formation by the removal of the methyl group seems more likely.

Irradiated isobutyramide gives a complex spectrum when irradiated. The two spectra shown in Figures 36A and 37A, while not identical, both give similar results. Using the four outer lines of the spectra, each has been fitted with the seven-line theoretical spectrum shown in Figures 36A and 37A, and having the related parameters given in Table VI. These spectra have line intensity ratios 1:6:15:20:15:6:1, and the radical indicated below having six equivalent hydrogen nuclei is suggested as that responsible for these lines.



$$\cdot\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-NH_2$$

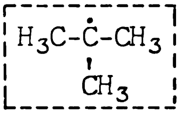
Figures 36B and 37B show the remaining spectrum after subtraction of the appropriate theoretical seven-line spectra from 36A and 37A respectively. These are patterns of four lines with intensity ratios of 1:3:3:1, such as would be predicted for a $\cdot CH_3$ radical. These lines were matched as well as possible using a combination of four individual peaks of the appropriate height. Parameters for these peaks are given in Table V also, and the curves are indicated on the spectra.

The isobutyramide sample which gave the spectrum in 36A was accidently warmed. It was then kept in liquid air for three days, and rerun at -183°C. The resulting spectrum is shown in Figure 38. This is an almost perfect, resolved seven-line spectrum.

It would appear from these results that the radical with six equivalent hydrogens is the more stable radical. The other species, presumably $\cdot CH_3$, is perhaps formed immediately upon irradiation, but readily recombines in some manner so as to leave only the more stable species. The breaking of a C-C bond leaves the further question of what has become of the extra unpaired spin remaining on the larger fragment after separation of the methyl. Such a fragment would be expected to give a further five-line spectrum but this is not observed.

Trimethylacetamide also gives a complex spectrum. Of the many lines present, eight of the main lines have been identified as the central lines of a ten-line spectrum having intensity ratios 1:9:36:84:126:84:36:9:1. The spectrum is shown in Figure 39, and the parameters measured are in Table V. The first and tenth lines do not appear, but as their intensities are of the same order of magnitude as the noise level present, this is not surprising.

The observed lines could only be produced by a radical having nine equivalent hydrogen nuclei. To obtain such a radical, radiation damage must break the C-C bond to the carbonyl group in the molecule. The suggested radical is:



$$H_3C\text{-}\dot{C}(CH_3)\text{-}CH_3$$

The remaining lines of the spectrum could not be resolved, and therefore it is not possible to conjuecture what other type of radical is present. Several sources of further radicals are possible; the initial breaking of a C-H bond or of a different C-C bond, the breakdown of the C_4H_9 radical mentioned above, and the interaction of the electron remaining on the amide fragment with the H or N nuclei therein. The relative intensities of the two sets of lines does appear to vary with both the conditions of irradiation and the temperature at which the spectrum is recorded.

Isobutyric acid gives a complex spectrum, which contains a dominant series of seven lines of intensity ratios 1:6:15:20:15:6:1. The spectrum is shown in Figure 40 and the related parameters in Table V. In this case the radiation damage must break a C-H bond and form a radical similar to the more stable radical formed from isobutyramide, which has six equivalent hydrogen nuclei.

Irradiated pivalic acid (trimethylacetic acid) gives a complex spectrum similar to that of trimethylacetamide. Again the eight dominant lines are best matched by a ten-line theoretical spectrum with intensity ratios 1:9:36:84:126:126:84:36:9:1, as shown in Figure 41. This pattern is presumably due to the same radical as suggested for trimethylacetamide. The remaining lines of the spectrum could not be resolved.

Only one compound having two different substituents on the nitrogen, N-butyl-N-methylformamide, was studied. The resulting spectrum is shown in Figure 42. It is quite apparent from the form of this spectrum that more than one radical is present. A theoretical spectrum was not determined to match this experimental result.

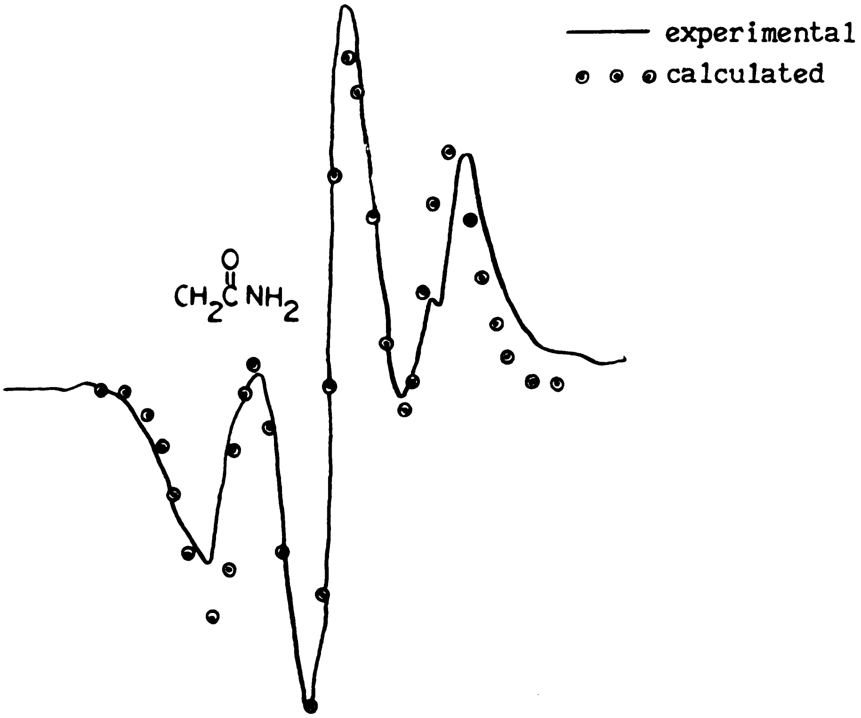


Figure 33. Experimental spectrum of acetamide and the matching theoretical spectrum.

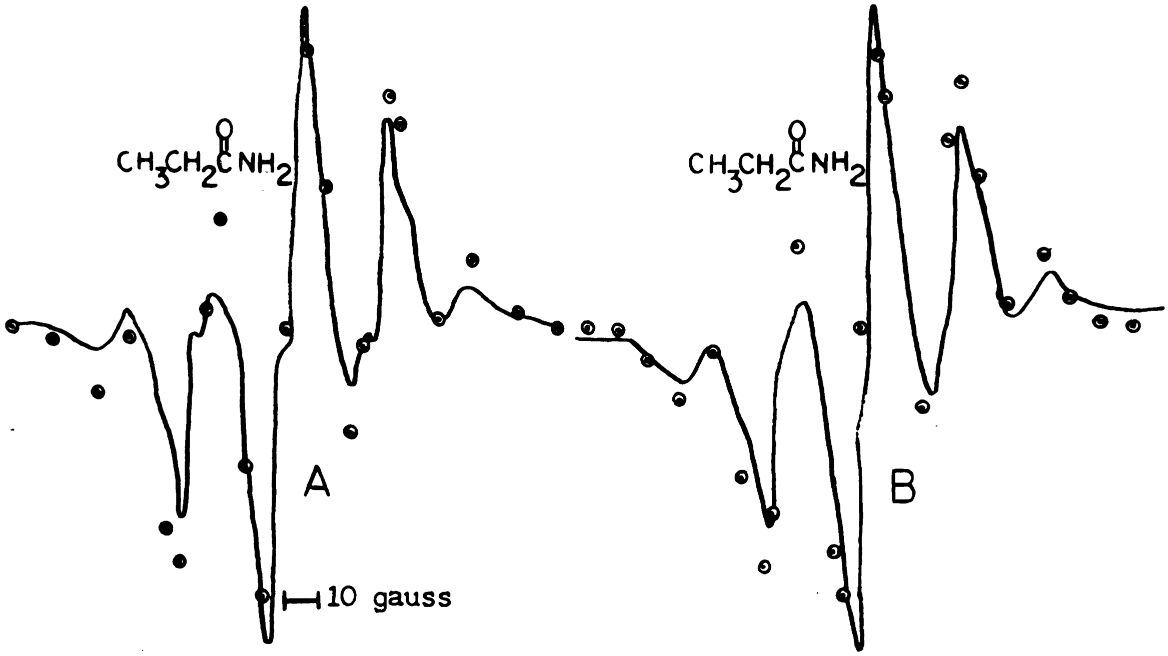


Figure 34. Experimental spectra of propionamide and the matching theoretical spectra. A. As recorded by K. R. Way. B. As recorded by P. S. Rao.

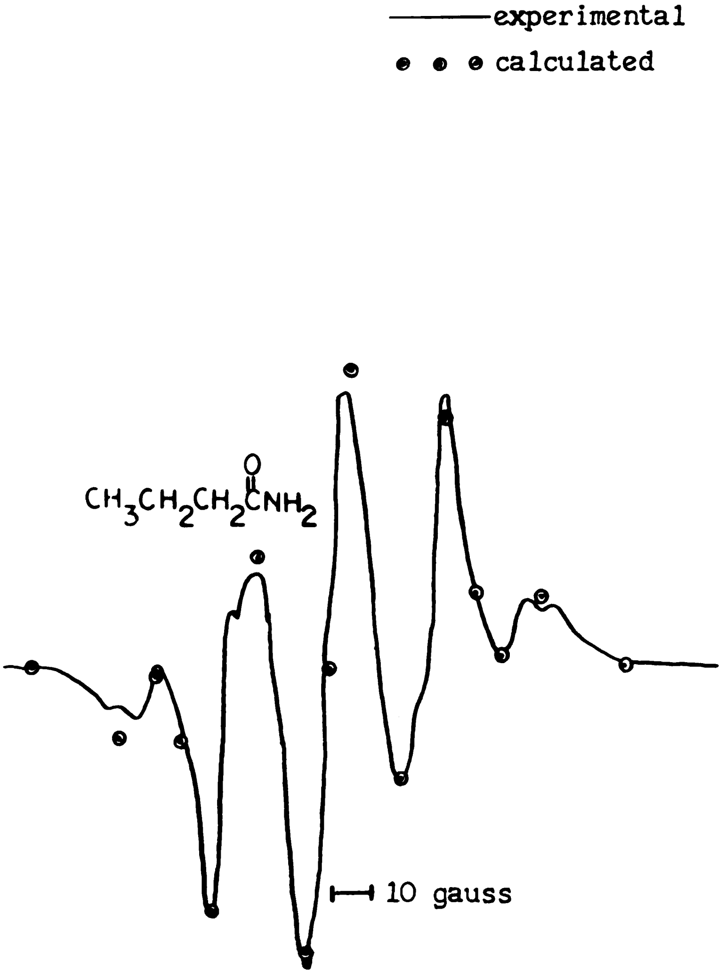


Figure 35. Experimental spectrum of n-butyramide and the matching theoretical spectrum.

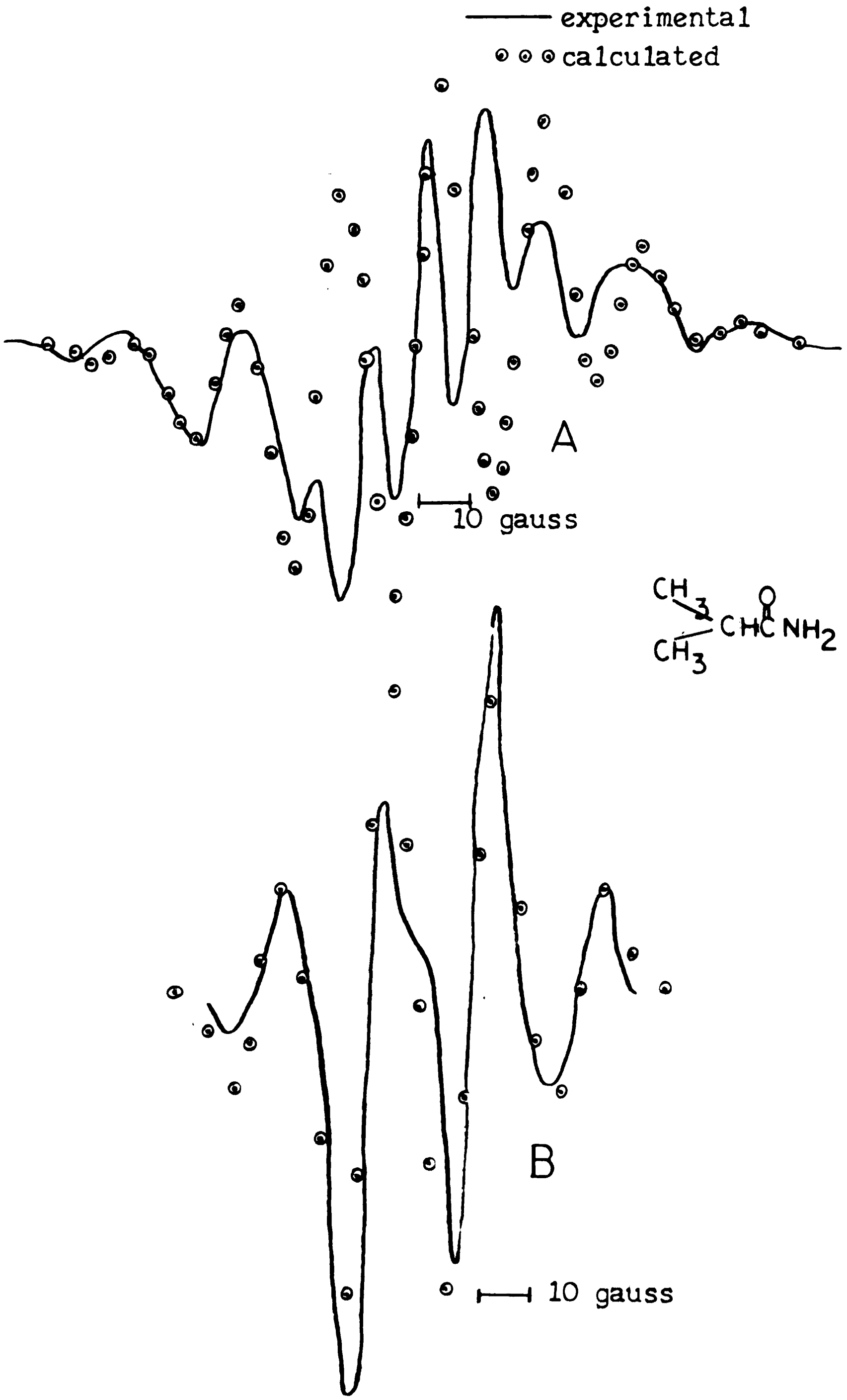


Figure 36. Experimental spectrum of isobutyramide recorded by K. R. Way and the matching theoretical spectra. A. Total experimental spectrum as recorded by K. R. Way, and the theoretical seven-line spectrum. B. Difference spectrum obtained from 36A and the theoretical four-line spectrum.

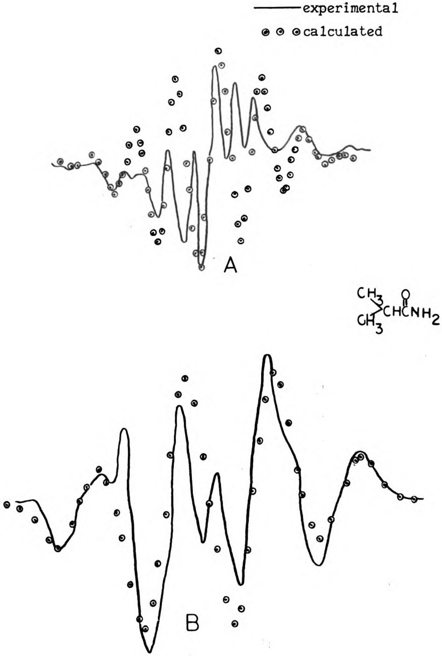


Figure 37. Experimental spectrum of isobutyramide recorded by P. S. Rao and the theoretical matching spectra. A. Total experimental spectrum as recorded by P. S. Rao, and the theoretical seven-line spectrum. B. Difference spectrum obtained from 37A, and the theoretical four-line spectrum.

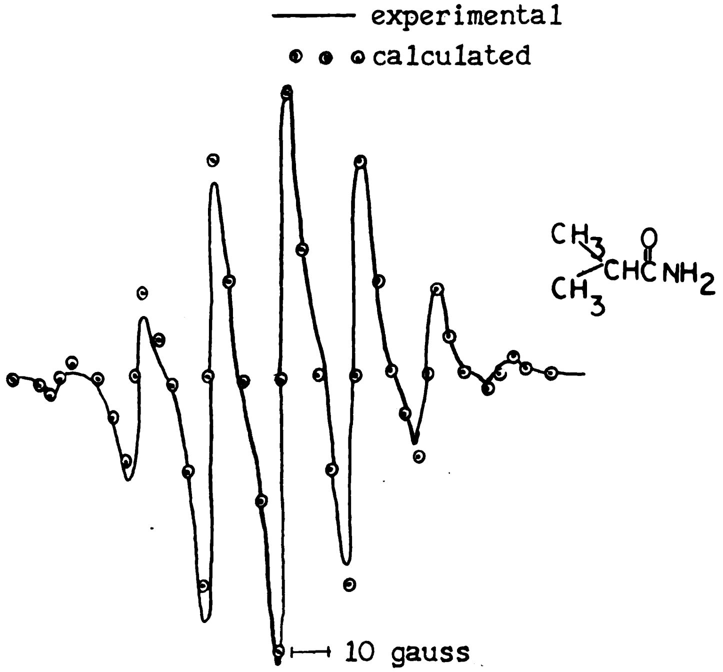


Figure 38. Experimental spectrum of aged isobutyramide and the matching theoretical spectrum.

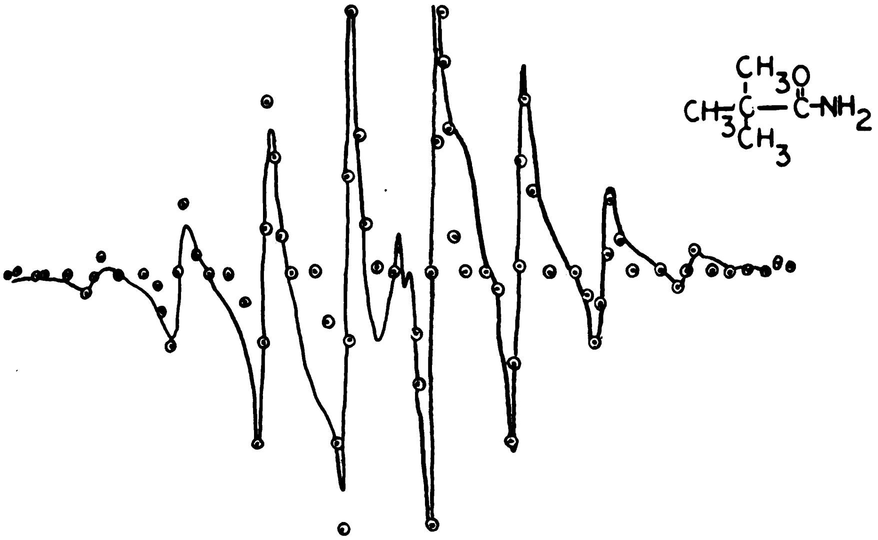


Figure 39. Experimental spectrum of trimethylacetamide and the matching theoretical spectrum.

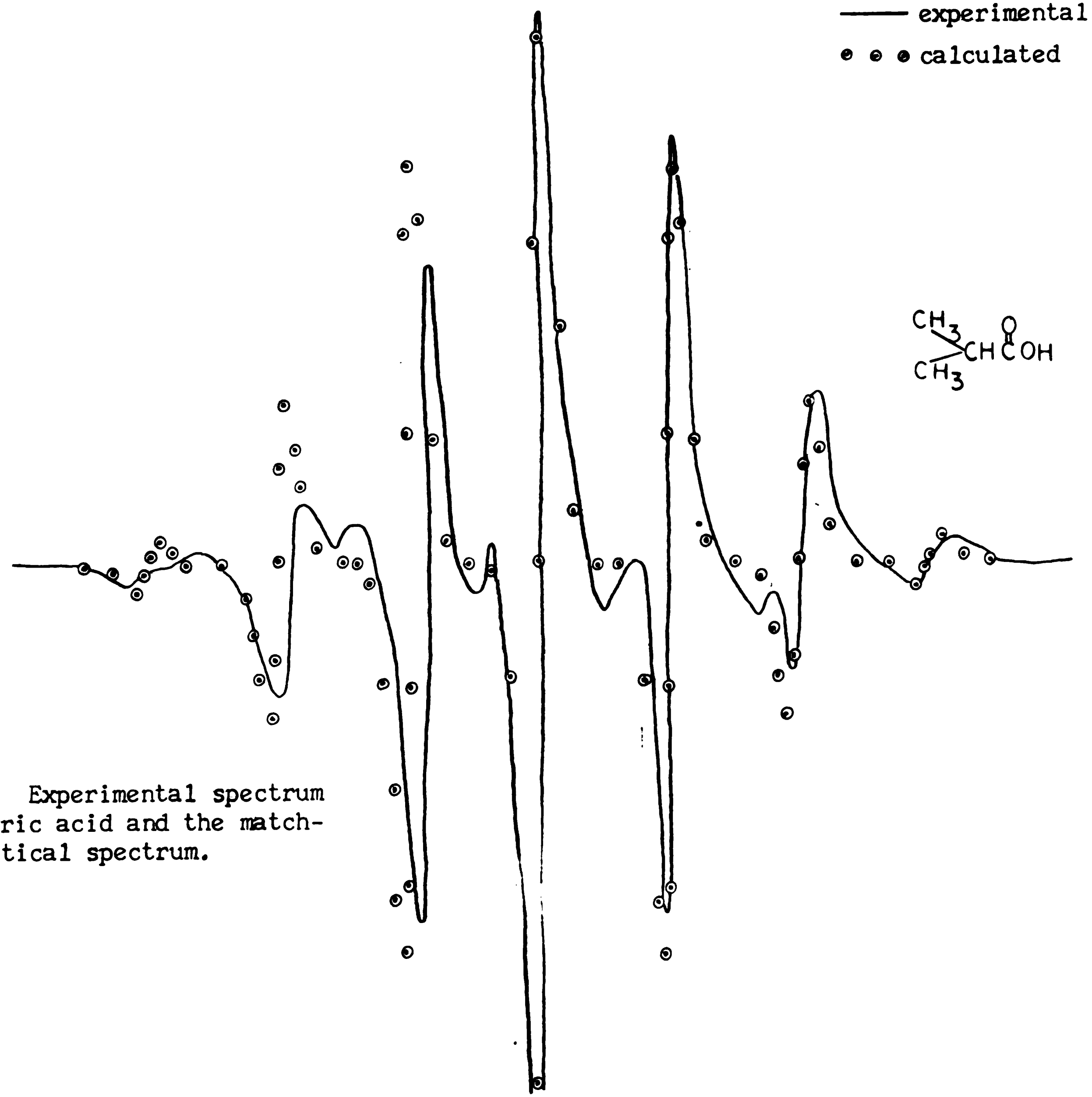


Figure 40. Experimental spectrum of isobutyric acid and the matching theoretical spectrum.

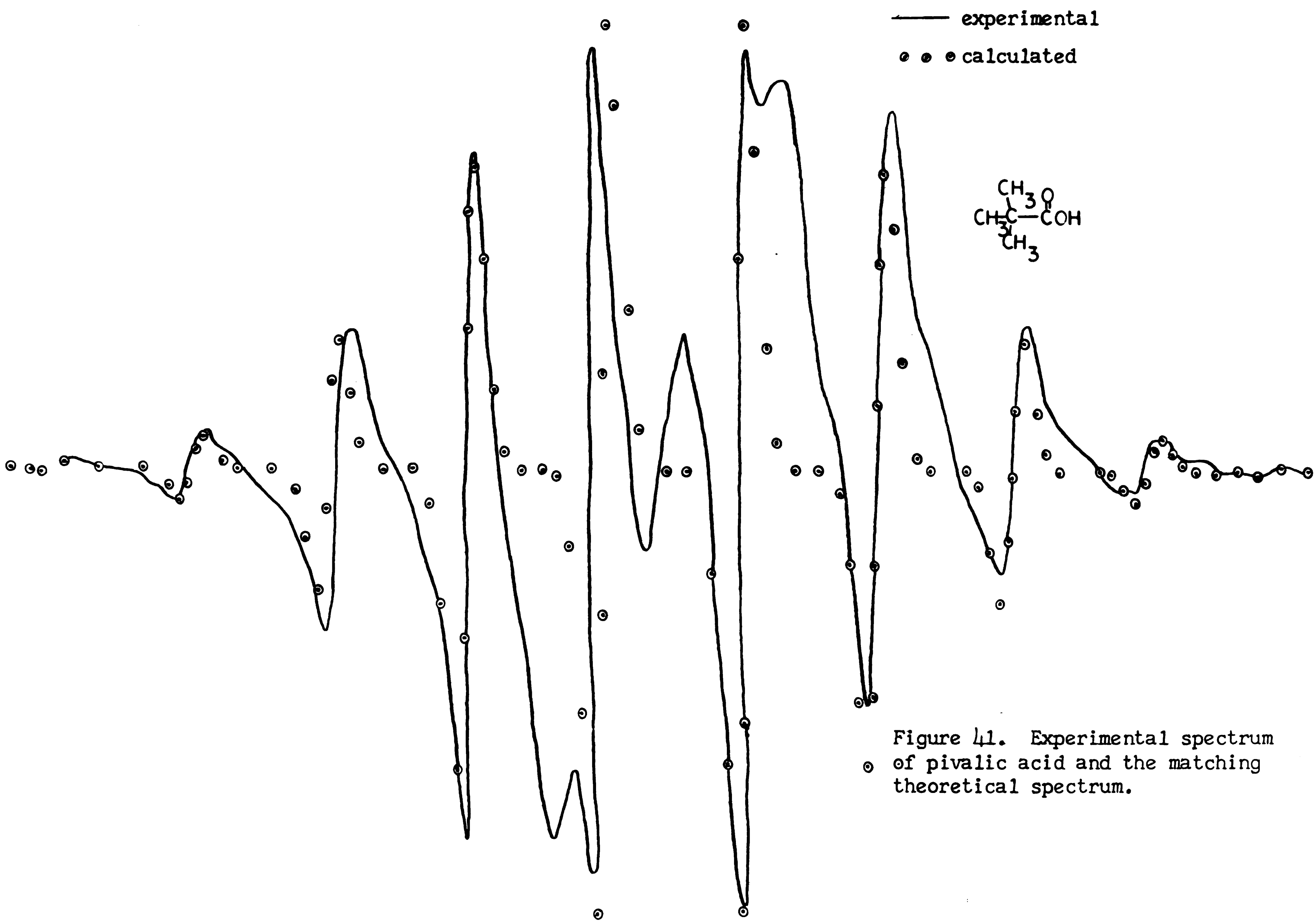


Figure 41. Experimental spectrum of pivalic acid and the matching theoretical spectrum.

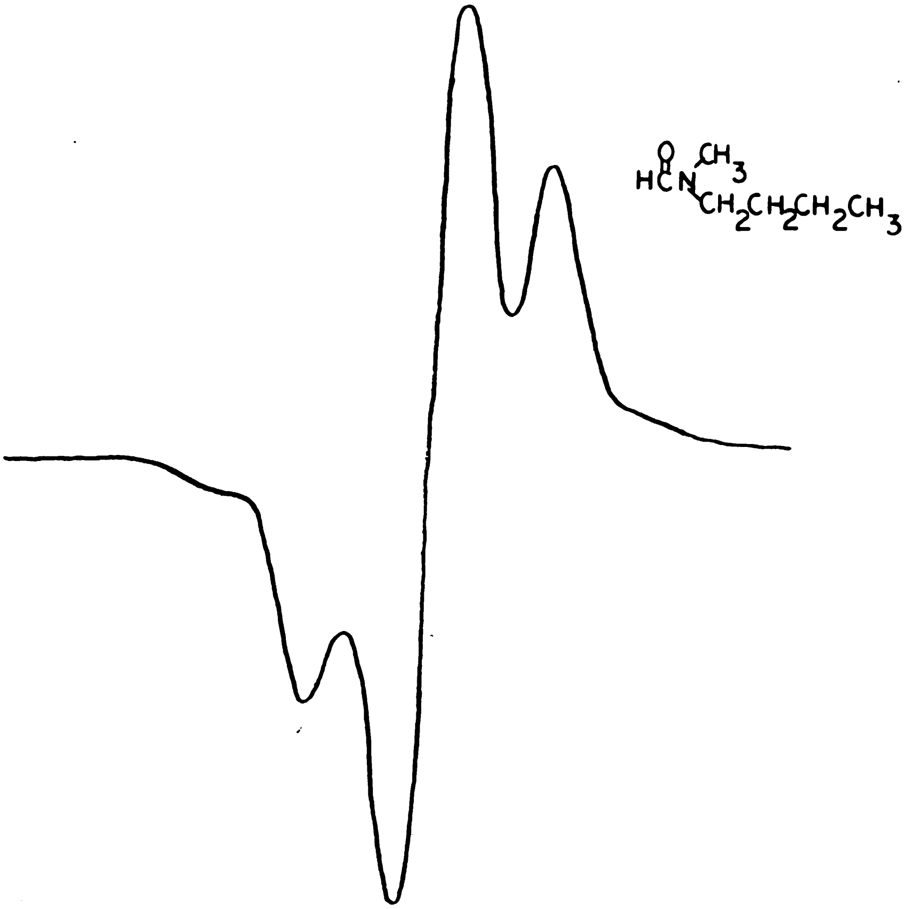


Figure 42. Experimental spectrum of N-butyl-N-methylformamide.

Table V. Parameters of the E.S.R. spectra of irradiated amides and carboxylic acids.

Compound Irradiated	No. of lines	Line width (gauss)	a peak spacing (gauss)	ratio a/lw	rec'd by	Shown in Figure
Acetamide	3	---	---	1.36	Rao	33
Propionamide	5	17.25	24.7	1.43	Way	34A
Propionamide	5	---	---	1.57	Rao	34B
n-Butyramide	5	15.8	22.6	1.425	Way	35
Isobutyramide	7	15.3	23.6	1.54	Way	36A
	4	9.6	21.6	2.25	Way	36B
Isobutyramide	7	---	---	2.00	Rao	37A
	4	---	---	2.00	Rao	37B
Isobutyramide (aged)*	7	6.5	19.6	3.00	Way	38
Trimethylacetamide	10	---	---	5.54	Rao	39
Isobutyric acid	7	---	---	4.90	Rao	40
Pivalic acid	10	---	---	5.25	Rao	41

*Error for this spectrum only is estimated at ± 2 gauss.

DISCUSSION

The radical produced by the irradiation of an N-alkylamide is found in all cases to be the result of the removal of a hydrogen from the substituent on the nitrogen atom. A carbon-hydrogen bond of CH_2 or CH is broken in preference to one of CH_3. The alpha-carbon also tends to have as many beta-hydrogens as possible.

The identification of the radical produced from irradiated N-methylamides may be based on three factors. (i) Since all compounds of this type studied give similar spectra, it is reasonable to assume that all radicals formed are similar. (ii) Except for the substituted acetamides, damage in the hydrocarbon group bonded to the carbonyl group would have to break a carbon-carbon or a carbon-chlorine bond to produce a radical which would give a three-line spectrum. By comparison to the previous results on irradiated organic compounds, we find this to be less likely than the breaking of a carbon-hydrogen bond in most cases. (iii) Luck and Gordy[48] have observed a coupling constant of 23 gauss for irradiated acetamide, which gives a radical similar to the other possible ones for N-methylamides. This value is considerably larger than those found here, which vary from 16.8 to 19.6 gauss. Thus radical formation for N-methylamides by removal of a hydrogen from the carbon atom bonded to the nitrogen seems definite.

N-Ethylamides produce a radical giving a five-line E.S.R. spectrum. Only in the case of the substituted butyramides in this series could such a spectrum arise from damage at any site other than in the N-ethyl group. This would again necessitate the less likely removal of a methyl group, and would leave a radical similar, but not identical to that believed to be produced from irradiated propionamide. The coupling constant observed, 20.1, for N,N-diethylbutyramide, again is considerably smaller than that for the radical from propionamide which is 24.7 gauss. The validity of this argument is reduced by the fact that for the two radicals compared the unpaired electron is assumed to be on different carbon atoms. From the similarity of the appearance of the spectra and the constancy of the observed coupling constant in radicals obtained from N-ethylamides, (20.1 to 20.6 gauss), it seems likely that the same radical is produced in each case.

We have assumed that the proton is removed from the CH_2 rather than the CH_3 in the ethyl group. This assumption is based on the observed difficulty of proton removal from methyl groups in general, but we cannot say with certainty that this is the site of radiation damage. To verify the selection, studies of the spectra of irradiated single crystals or studies of deuterated compounds are required.

Amides having as nitrogen substituents either normal propyl or isopropyl groups all give seven-line E.S.R. spectra after irradiation. All of these radicals must result from the removal of a proton from the central carbon atom of the propyl group if interaction with the odd electron is assumed to be limited to alpha- and beta-protons. As mentioned above, gamma-proton interaction has been observed, but is much too small to be observable with the large line widths found here. Once again the coupling constants observed, 18.4 for an *n*-propyl substituent and about 22.5 gauss for an isopropyl substituent are smaller than that for the seven-line spectra for radical sites on the carbonyl side, (22.6 and 23.6 gauss), but the difference is not as great in this case.

Burrell[66] recorded a four-line spectrum for N-n-propylamides and also for N-n-hexylamides, which indicates that a proton is removed from the CH_2 group adjacent to nitrogen. He also irradiated a sample of N-n-propylpropionamide which had deuterium substituted for both protons on the central carbon of the nitrogen substituent. The radical thus formed gave an E.S.R. spectrum of two broad lines consistent with his results.

Our seven-line spectrum indicates removal of a proton from the CH_2 group next to the terminal CH_3 group. Burrell[67] did find a seven-line spectrum for a radical in irradiated tetra—n-butyl ammonium salts, and Smaller and Matheson[59] observed seven lines in the spectra of irradiated long, straight-chain alkanes, as did Alger, Anderson and Webb[60] for n-propyl ether. Burrell has suggested that in these cases the proton was removed from the CH_2 next to the methyl group because of the additional 'resonance' stability which is to be gained through the added hyperconjugation possible in this form. This reasoning does indeed seem to give a valid argument for the formation of the 'seven-line' radical, but the explanation of the differing results obtained for N-n-propylamides is not clear.

Another possibility for the seven lines observed in our study for N-n- propylamides is molecular rearrangement after initial radical formation to form a secondary radical identical to that formed by the irradiation of N-isopropylamides. We feel, however, that the comparatively large difference in observed coupling constants (18.4 gauss for N-n-propylacetamide and 22.1-22.7 gauss for N,N-diisopropylacetamide) makes it unlikely that these two form the same radical. Single crystal studies would help to elucidate the structure of the radical formed, since one could differentiate between alpha- and beta-proton interactions in this way.

The presence of a second substituent on the nitrogen apparently has no effect on the radical formed, or on the observed coupling constant as long as both substituents are the same. As seen for N-methyl-N-butylformamide, mixed substituents give mixed radicals. A study of amides with more widely varied mixed substituents might produce interesting data on preferred damage sites.

In no case is any interaction observed either with the nitrogen or with any nucleus 'across' the nitrogen bridge from the radical site. This seems to be somewhat surprising, especially for N-methylamides, where one might expect to observe interaction of the hydrogen bonded to the nitrogen with the electron spin.

Most of the amides without nitrogen substituents form radicals by the removal of a hydrogen atom from the alkyl group; in one case a carbon-carbon bond is broken in the alkyl radical. Once again a primary carbon is a less likely point for attack than a secondary or tertiary carbon.

Acetamide gives the three-line spectrum previously observed by Luck and Gordy,[48] due to the radical formed by the removal of a proton from the CH_3 group. The five-line spectrum from irradiated propionamide also agrees with that found by Luck and Gordy. The coupling constant, 24.5 gauss, recorded by them agrees well with our value of 24.7 gauss.

The spectrum observed for irradiated *n*-butyramide, a quintet, is most puzzling. Considering the results of Tsvetkov, Rowlands, and Whiffen[51] for irradiated acids, we tend to believe that a CH_3 group is removed from this compound by irradiation, since they found that in no case was a proton removed from a primary carbon. Luck and Gordy also studied n-butyramide, but were unable to explain the quintet they recorded which they identified as a pair of overlapping triplets.

It is interesting to observe that among irradiated alconols studied by E.S.R., n-propanol is the one for which the radical is most in doubt. The same alkyl group is available for attack in n-butyramide and n-propanol. This same alkyl group is also the one for which we observed a seven-line spectrum when it was on the nitrogen, but Burrell found only four lines. It would appear that this particular grouping may have several points of attack which are very nearly equivalent. Perhaps small amounts of differing impurities or very small differences in experimental conditions among various studies could be the determining factor in such a case.

The isobutyramide spectra show clearly the preferential removal of a proton from a tertiary rather than a primary carbon. Even the carbon-carbon bond of the methyl group is more readily broken than any carbon-hydrogen bond on it. Since the radical responsible for the seven-line spectrum has no alpha-protons interacting, it is somewhat surprising that the observed line widths are not narrower in the combined spectrum. It appears that a methyl radical can move through the lattice readily, and thus its rapid decay, probably by combination, at a slightly higher temperature is not surprising. The change in the coupling constant observed in the aged sample is not readily explained. It may be the result of the large experimental error in this particular spectrum.

The ten-line spectrum observed for irradiated trimethylacetamide again shows the difficulty of removing a proton from a methyl group, with the preferential breaking of the carbon-carbon bond to the carbonyl group. The remaining amide fragment would surely seem unstable, and some recombination or rearrangement is likely to occur soon after its formation.

The two acids studied give spectra and apparently also radicals similar to the comparable amides. This is usually found to be the case for analogous amides and acids. The ammonium salt of pivalic acid has been studied in polycrystalline and single crystal form by Tsvetkov, Rowlands and Whiffen. Their results are similar to those presented here, and they have determined a coupling constant of 23 gauss, which is typical of methyl-proton interaction with the electron spin. They also observed some further complexity in single crystal spectra which they could not explain.

As was observed in the review of results from the study of other irradiated hydrocarbon compounds, branching increases the complexity of the spectra recorded. We have found the same to be true for amides. This undoubtedly results from a greater number of possible points of attack, thereby producing small amounts of radicals other than the main one. Only in one case, that of isobutyramide, were we able to distinguish two separate radicals.

The general trend observed of a smaller coupling constant for radicals of alkyl groups on the nitrogen than for the same groups on carbonyl seems to indicate a greater delocalization of the unpaired electron by the nitrogen than by the carbonyl group. Presumably some of the spin density is moved from the alpha-carbon toward the nitrogen. The fact that the effect is less noticeable as the size of the group increases is consistent with this idea, and we would not expect the difference to be noticeable in a chain of four or more carbons, assuming the removal of a proton from the group adjacent to the terminal methyl group. If the difference in the coupling constants observed here is significant, it will be most valuable in further identification of radical sites.

All of the proposed sites of spin concentration are consistent with the generalizations set forth by Tsvetkov, Rowlands and Whiffen[51] for acids, except that they always found a proton to be removed from the CH_2 next to the carbon double bonded to oxygen. _n_-Butyramide once again does not conform to this. Since similar results are always found for analogous amides and acids, such correlation of results is excellent verification of our results.

In all of the suggested radicals, the molecule is shown as remaining intact except for the specific bond broken to form the free radical. No interaction has been observed for any part of the molecule other than the alkyl group attacked. Therefore we cannot state with certainty that further disintegration of the molecule has not occurred. There is, however, chemical evidence[69-73] to assert that the breaking of a single bond is the usual result in radiation damage. We have no reason to believe that more than one bond in any given molecule should be broken, although the energy involved in 1 Mev. electron irradiation is certainly sufficient to break any chemical bonds. If other damage does occur, it would seem unlikely that the large fragments which would have to remain in most cases would be able to move through the lattice readily, and therefore recombination would probably be immediate.

The value of g was not specifically measured, but was close to the free-electron value of 2.0023 in all cases.

SUMMARY

A series of amides and carboxylic acids have been irradiated with 1 Mev. electrons at liquid air temperature, and their E.S.R. spectra recorded. The spectra observed are used to identify the radicals formed and to suggest a scheme for the prediction of the site of radiation damage in such compounds. Hyperfine coupling constants for the protons of these radicals have been measured.

In most cases a hydrogen is removed from one of the alkyl groups by the radiation. An alkyl group on the nitrogen is always attacked in preference to a group attached to the carbonyl carbon. In some cases a carbon-carbon bond is broken rather than a carbon-hydrogen bond. We have observed no other type of radiation damage.

The particular site of hydrogen removal within the alkyl group is found to be consistent with the following generalization: (1) a methyl carbon hydrogen bond is broken only if no other carbon-hydrogen or carbon-carbon bond is present in the preferred alkyl group, (2) a proton is removed from a CH_2 group next to a methyl group in preference to a similar group adjacent to the nitrogen, (3) for a tertiary carbon the carbon-carbon bond to the carbonyl group is broken in preference to the carbon-carbon bond to a methyl group.

Radical formation can be accurately described by these generalizations for N-substituted amides, but some anomalies appear when the only alkyl group present is adjacent to carbonyl. The radical formed from n-butyramide cannot be identified with certainty, but carbon-carbon bond breakage and loss of the terminal methyl group is suggested.

For isobutyramide significant amounts of two radicals appear to be present, with either a methyl group of a hydrogen atom being removed from the tertiary carbon adjacent to the carbonyl group. The radical formed by the loss of hydrogen is the more stable. Irradiated isobutyric and trimethylacetic acids give the same radical as the analogous amide.

Substitution of two different types of alkyl groups on the nitrogen gives the only other example observed of the formation of sibnificant amount of more than one radical. Branched alkyl groups give some extra spectral lines which could not be identified accurately, but which probably indicate the presence of small amounts of radicals other than the predominent species identified. The presence of two substituents of the same kind on nitrogen has no significant effect on the site of radiation damage or on the spectrum observed. Interaction with the unpaired electron spin is limited to alpha- and beta-protons in the alkyl group attacked.

In all cases the coupling constant observed for an alkyl radical on nitrogen is smaller than that for a similar alkyl radical bonded to the carbonyl. Thus N-methylamides give a value of 16.8 to 19.6 gauss, while the generally accepted coupling constant for acetamide is about 23 gauss. N-ethylamides give a coupling constant from 20.1 to 20.6, while that of propionamide is 24.7 gauss. This difference indicates that some of the unpaired electron spin is localized on the nitrogen atom, even though no interaction from this nucleus is observed.

We feel that these results will give significant assistance in the identification of radicals in future studies of irradiated organic molecules.

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