national Table the atomic weight of fluorine (which has no known natural isotopes) is given as 19.00, but its more exact value is 18.9992 ± 0.0002.[1] The adoption of the exact number 19 for fluorine therefore would shift all numbers related to the current chemical scale upward by only about one part in 25,000. A change of this magnitude could be neglected for most of the data of chemistry, and the formal revision of books, etc., could proceed leisurely, with little confusion. On the current physical scale the mass of F^{19} is 19.0044. A change to 19 would shift all masses on the physical scale downward by about two parts in 10,000, an amount that would, of course, necessitate revision of all tabulations. Provided it offers no insurmountable obstacles for intercomparison with the masses of other nuclear species, a scale based on $F^{19} = 19$ might be more acceptable to physicists than one based on a non-integral value such as 15.9956 for O^{16}.

If a decision can be reached to unify the chemical and physical scales by one means or another, it would probably be desirable to set some fixed future time at which the change-over will be made, so as to give authors, editors, and publishers adequate notice. If such a decision is not reached, all possible measures should be taken to minimize confusion and misunderstanding. In considerable areas of scientific work the context will indicate clearly the scale that is being used. For example, all data on the masses of individual nuclear species and quantities related to them would be recognized as based on the physical scale. Likewise, all the conventional atomic and molecular data of chemistry would be recognized as belonging to the chemical scale. In borderline areas, such as matters concerning the Faraday, or Avogadro's number, it should be possible to establish a uniform practice to use always one scale or the other. Some well-planned and conscientious efforts of this kind might make the situation tolerable.

It remains only to repeat the invitation to all concerned to give the problem thorough and objective consideration. Expressions of opinion will be welcomed.

U. S. BUREAU OF STANDARDS
WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

Effects of X-Irradiation upon Some Organic Substances in the Solid State: Simple Alcohols, Amines, Amides and Mercaptans[1]

BY CLARENCE F. LUCK AND WALTER GORDY

RECEIVED DECEMBER 19, 1955

Microwave magnetic resonance has been employed to study the effects of ionizing X-rays on some simple alcohols, amines, amides and mercaptans in the solid state. The proton hyperfine structure of the electron spin resonance allows fairly definite identification of the radicals produced in certain of these. For example, methyl alcohol, acetamide, sodium methoxide appear to form the radical $(CH_2)^+$, which, however, could be attached to some other molecule or group provided that the group has no nuclei which could interact with the electron spin. Ethyl alcohol and propionamide appear to form the radical $(C_2H_4)^+$. No such radicals are formed by the sulfur compounds, and it is believed that the odd electron (electron vacancy) in these remains on the S atom or atoms.

Microwave paramagnetic resonance has been used in this Laboratory to study the effects of ionizing radiations on many substances including amino acids,[2] proteins, carboxylic acids and metal organic compounds. A number of organic free radicals have been produced and identified in the solid state. A set of microwave "fingerprints" of organic radicals is thus being obtained which allows recognition of these same radicals when they are produced in other substances. In addition, experience is being gained which helps in the prediction of the primary effects of ionizing radiation in complex organic substances. The present work represents an extension of the method of microwave magnetic resonance to other classes of organic compounds.

The experimental methods are the same as those employed in the previous work.[2] The samples were irradiated several hours with 40 kv. X-rays Most of the samples of the present study were studied at 77°K. and at 9 kMc./sec.

A general tendency already noted[2] previously is that whenever a given molecule of a solid is dissociated by ionizing radiations, the various parts, unable to escape rapidly, tend to react and re-react until the most stable assembly of simpler molecules and radicals is formed from the pieces. This useful generalization is borne out by several examples in the present study. The resonance of ethyl alcohol (see Fig. 1) consists of the characteristic quintet of the ionized ethylene radical $(C_2H_4)^+$. It is evident that in addition to $(C_2H_4)^+$ the stable H_2O molecule could be formed from ionized C_2H_5OH. Although the heat of formation of the $(C_2H_4)^+$ radical is unknown, its paramagnetic resonance pattern shows that the odd electron is in a symmetric molecular orbital which is spread all over the molecule. This delocalization of the odd electron wave function should enhance the stability of this radical over one of lower symmetry in which the odd electron would be essentially localized on a carbon.

A quintet like that for irradiated ethyl alcohol is found for irradiated propionamide and presumably it arises from the same radical, $(C_2H_4)^+$ (see Fig. 2). The spacing is slightly different, total spread 98 instead of 93 gauss. If this small difference is not due to error, it may arise from differences in internal

---

[1] This research was supported by The United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] W. Gordy, W. B. Ard and H. Shields, *Proc. Nat. Acad. Sci.*, **41**, 983 (1955); **41**, 996 (1955).

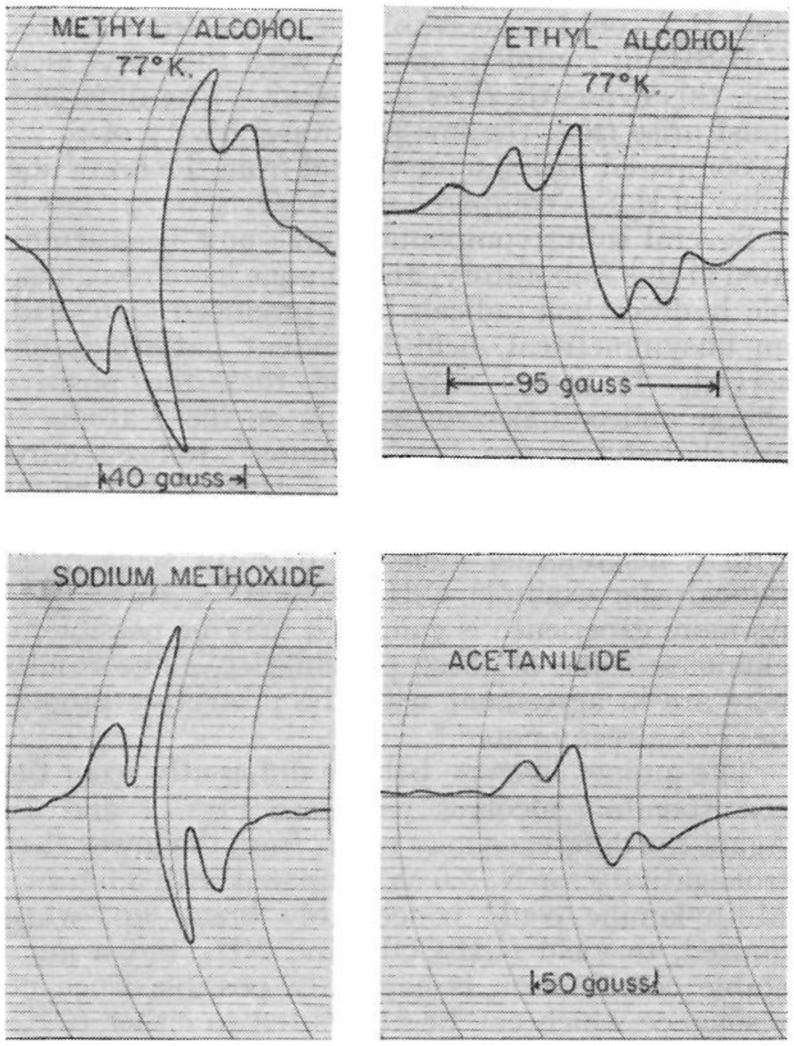


Fig. 1.—Tracing of electron-magnetic resonance spectra of X-irradiated methyl alcohol, ethyl alcohol at 77°K. and of sodium methoxide and acetanilide at room temperature. The curves represent the first derivatives of the actual absorption lines. A phase-sensitive, lock-in detector was employed with magnetic modulation of the absorption line at the lock-in frequency. The *g* factor for the center of the multiplets is essentially that for the free electron spin. The observation frequency is 9 kMc.

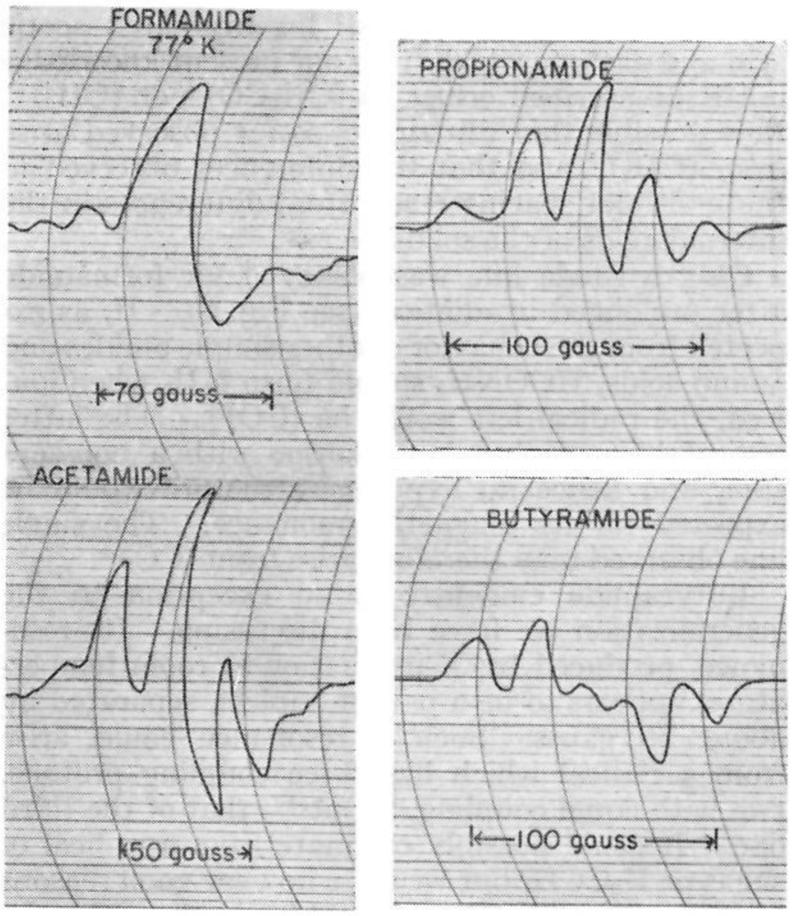
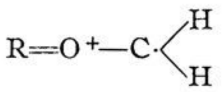


Fig. 2.—Tracing of electron-magnetic resonance spectra of X-irradiated formamide at 77°K. and of propionamide, acetamide and butyramide at room temperature, with conditions as described for Fig. 1.

fields of the two solids. Such small differences were observed in the previous work. The formation of $(C_2H_4)^+$ from ionized propionamide, $(C_2H_5CONH_2)^+$, is in accord with the above generalization, for it would leave groups from which the very stable NH_3 and the fairly stable CO could be formed. Alternatively, $(C_2H_4)^+$ and $HCONH_2$ could be formed. The identical quintet is obtained by irradiation of alanine[2] from which the stable molecules NH_3 and CO_2 can be formed in addition to the $(C_2H_4)^+$.

From the previous results one would expect ionized methyl alcohol $(CH_3OH)^+$ to break up and form the highly stable H_2O and the radical $(CH_2)^+$. This expectation is borne out by the triplet proton hyperfine structure of the observed resonance (Fig. 1). This triplet with intensity ratios (1, 2, 1) indicates equal coupling of the odd electron spin to 2, and only 2, proton moments. The total spread of this triplet, 30 gauss, is the same as that in Fig. 1 for irradiated sodium methoxide, CH_3ONa. Evidently the latter molecule does not form water when irradiated but rather sodium hydroxide. If H_2O were formed, the remaining parts, CH and Na^+, could not give the observed pattern. One might assume, of course, that two or more molecules are involved and that when the radical is formed it immediately attacks a neighboring molecule to form something else. Chain reactions no doubt occur in many irradiated substances, and they are probably responsible for the absence of detectable resonances in certain substances which we have irradiated. We are inclined, however, to postulate the simplest mechanisms which will account for the observations.

As might be expected, the total spread of the pattern of a given radical is not exactly the same in different solids. Quintets in several irradiated solids believed to arise from $(C_2H_4)^+$ have been observed with multiplet spreads always between 90 and 100 gauss. It seems unlikely that this radical could form any kind of bond to a neighboring molecule without destroying the symmetry of its hyperfine pattern. Unlike $(C_2H_4)^+$, however, the $(CH_2)^+$ could form a bond to something—say an O of an R=O group—to make a radical such as



$$\mathrm{R{=}O^{+}{-}C\cdot\!\!\begin{array}{l}\diagup \mathrm{H}\\ \diagdown \mathrm{H}\end{array}}$$

which would always give a symmetrical triplet resonance provided that the R group had no nuclei which could couple to the electron spin. Symmetrical triplets have been observed in the present study and in the other work mentioned, with spreads ranging from 30 to 45 gauss. Thus we cannot be sure whether some or all of these arise from the free or from the bonded $(CH_2)^+$. In the case of irradiated acetamide (see Fig. 2) for which a spread of 45 gauss is observed, it seems probable that the ionized CH_3CONH_2 could break up to leave the radical $(CH_2CO)^+$ which could give the observed triplet and the stable NH_3 molecule. Also it might form $(CH_2)^+$, CO and NH_3. We cannot be sure which happens, particularly since 30 gauss triplets have been observed[2] for irradiated acetic acid and acetone which from our present knowledge might be ascribed either to $(CH_2CO)^+$ or $(CH_2)^+$. It is possible that all triplets so far observed arise from $(CH_2)^+$ and that the differences observed in the multiplet spacing result from differences in the internal fields of the solids.

Only a single line was observed for formamide after prolonged irradiation (see Fig. 2). If, as expected from the behavior of other simple amides and amino acids, $HCONH_2$ should form NH_3 when ionized, the radical left would be $(CO)^+$. The latter radical has no abundant isotope with a non-zero spin, and hence no hyperfine structure would be expected for its magnetic resonance. The single line observed may therefore arise from $(CO)^+$.

Butyramide evidently is an exception to the generalization we have been discussing. Its resonance, produced by X-irradiation at room temperature, appears to be a pair of triplets, separated by about 50 gauss. Such a resonance could arise from a radical which has three coupling protons, two with equal coupling, about $^1/_2$ that of the third one. It could possibly originate from a radical of the type H_2CCH, but we have no very good reasons for believing this radical would be produced by the irradiation.

From a comparison of Figs. 1 and 3, it is evident that ethyl mercaptan does not form the same radical under ionizing radiation as does ethyl alcohol. Nor does thioacetamide form the same radical when X-irradiated as does normal acetamide (compare Figs. 2 and 3.) We do not know what are the radicals found in the sulfur compounds, only that they are not the usual ones Although $(C_2H_4)^+$ and H_2S could conceivably be made from ionized C_2H_5SH, in complete analogy with the ethyl alcohol, this evidently does not occur. The difference must arise from the low electronegativity of S, 2.5 as compared with 3.5 for O, and from the lower stability of H_2S as compared with H_2O.

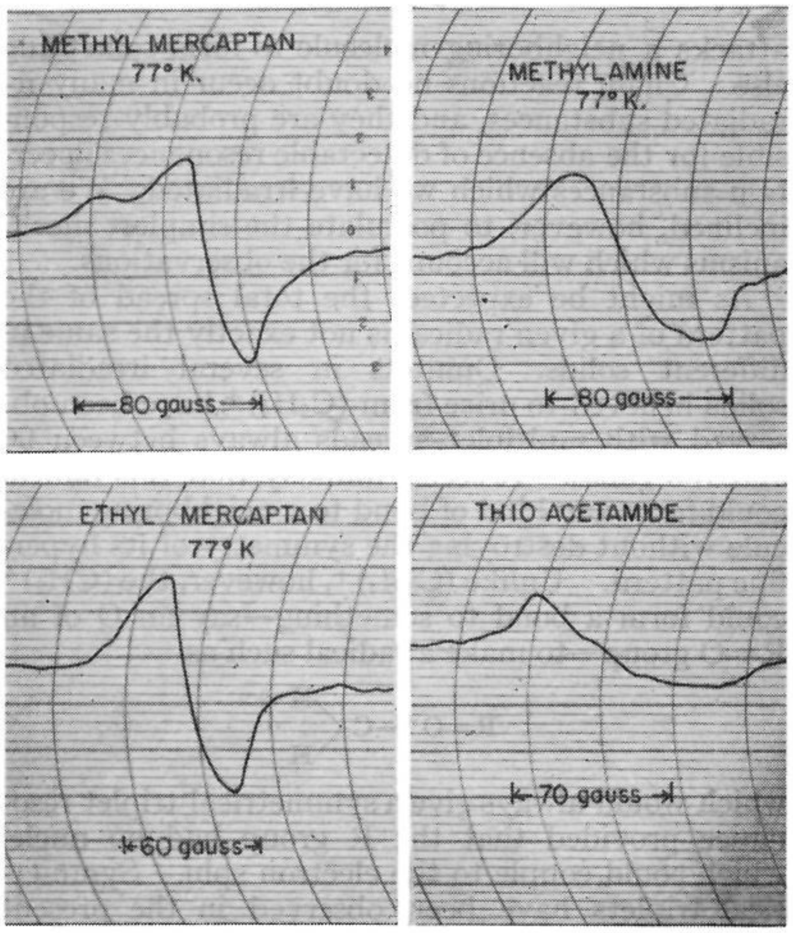


Fig. 3.—Tracing of the electron-magnetic resonance spectra of X-irradiated methyl mercaptan, ethyl mercaptan and methylamine at 77°K. and of thioacetamide at room temperature, with conditions as described for Fig. 1.

Several sulfur compounds have now been irradiated in this Laboratory, and in none have recognizable hydrocarbon radicals been produced. Instead, an unsymmetrical, field-dependent pattern is observed. It seems reasonable that the positive charge and odd electron remain on the S atoms or are shared between two S atoms. Ionized ethyl mercaptan might thus remain $C_2H_5S^+H$ or it might break up to form C_2H_4 and $(H_2S)^+$ or might react with a neighboring molecule to form some other radical—for example, $C_2H_5S \cdots S^+ C_2H_5$ and H_2. As more experience is gained, it may be possible to eliminate some of these possibilities. The results here are in agreement with the protective properties of S already noted.[2]

The amines likewise behave differently from the corresponding alcohols (compare Figs. 1 and 3). Again the difference may result from the lower electronegativity for N, 3.0 as compared with 3.5 for O. Methylamine could conceivably break up, when ionized, to yield $(CH_2CO)^+$ and NH_3, but a more stable combination is evidently possible since no resonance which can be attributed to either $(CH_2CO)^+$ or $(CH_2)^+$ is observed. The resonance for ethylamine was similar to that for methylamine.

Solid acetanilide, $C_6H_5NHCOCH_3$, when irradiated gives a triplet like that of irradiated methyl alcohol, see Fig. 1. This was a somewhat surprising observation for it would seem that the odd electron or electron vacancy would be trapped in the benzene ring. In several substances having aromatic rings studied in this Laboratory, a single resonance of about 20 gauss width is observed which is believed to arise from an odd electron trapped in the ring. Acetanilide is an exception. A possible explanation for the triplet is the $(CH_2)^+$ radical formed from the ionized acetanilide to leave the molecule C_6H_5NHCOH. It may be that the $(CH_2)^+$ becomes attached to the O of an adjacent molecule as previously explained, but of this we cannot be certain.

All, or nearly all, the resonances which we have observed in X-irradiated solids can be attributed with reasonable assurance to either positively charged or neutral radicals. We can give no equally convincing evidence for resonance of negatively charged radicals or F centers. We believe that in most instances the electrons which are knocked away in the ionization process are trapped at impurity centers or within the lattices where they give resonances too broad for detection with the small amplitude modulation method we employ.

It is of interest to compare the results obtained here on solids with the comprehensive work on liquid alcohols by McDonell and Newton,[3] who bombarded the liquid alcohol with 28 Mev. helium nuclei and analyzed the products with a mass spectrometer. The major products which they found

---

(3) W. R. McDonell and A. S. Newton THIS JOURNAL, **76**, 4651 (1954).

indicate rupture of bonds between the carbinol carbon and H, CH_3 and C_2H_5 groups, respectively, with the relative reactivity of these groups in the order $H > C_2H_5 > CH_3$. Thus for irradiated CH_3-OH the primary process in the liquid would presumably be the formation of H· and ·CH_2OH, with the formation of H_2O only a minor process. We believe that our findings differ from theirs mainly because of the more effective "caging" in the solid over the liquid rather than from the different type of bombardment. H atoms should have been detected in our experiments had they existed in amounts comparable to the other radicals found. Nevertheless, our results do not preclude the presence of small quantities of H atoms.

Acknowledgments.—We wish to thank Howard Shields and C. G. McCormick for checking some of these results at 23 kMc.

DURHAM, NO. CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

Microwave Investigations of Radiation Effects in Solids: Methyl and Ethyl Compounds of Sn, Zn and Hg[1]

BY WALTER GORDY AND C. GENE MCCORMICK

RECEIVED JANUARY 16, 1956

Microwave magnetic resonance spectra of the unpaired electrons have been used to investigate the effects of ionizing X-irradiation on frozen (at 77°K.) methyl and ethyl compounds of Zn, Hg and Sn. The $(C_2H_4)^+$ radical is believed to be produced from $Hg(CH_3)_2$, the C_2H_5 radical from $Hg(C_2H_5)_2$ and the CH_3 radical from $Zn(CH_3)_2$. The radical $(ZnCH_2)^+$ is apparently also produced in $Zn(CH_3)_2$ probably by a secondary reaction. The type of radical is indicated by the proton hyperfine structure of its electron spin resonance. From the spacing of the hyperfine multiplets information about the electronic structure of the radical is obtained. The radicals produced in $Sn(CH_3)_4$ could not be definitely identified, but one type appears to be $(C_2H_4)^+$.

Introduction

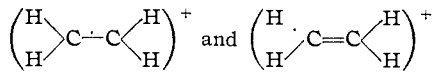
With microwave magnetic resonance of the unpaired electrons, we have studied the effects of ionizing X-rays on some simple organo-metallic compounds in the solid state. The results are in accord with the effects which might be anticipated from similar investigations recently made in this Laboratory on numerous other chemical and biochemical substances in the solid state. Certain of these results on amino acids and proteins,[2] carboxylic and hydroxy acids[3a] and plastics[3b] have been reported. Other reports are in preparation.

Experimental Method

The observations were primarily made at X band, ν = 9000 Mc./sec., but some were checked at 23,000 Mc./sec. A bolometer was employed for detection of the microwave power. The absorption line was magnetically modulated at 140 c.p.s. and was amplified at the second harmonic of this frequency. After preamplification, the signal was passed through a phase-lock-in detector and amplifier and was displayed on an Esterline Angus Recorder. The substances investigated are liquids at normal temperatures and pressures. They were all irradiated and observed in the solid state at the temperature of liquid nitrogen.

The small amplitude modulation and detection at the second harmonic of the modulation frequency give a signal which is the second derivative of the actual absorption line contour. The peak of the true absorption curve and the peak of the second derivative curve coincide, whereas the peak of the absorption curve appears at the "zero point" of the display of the first derivative employed in the other work.[3] Detailed descriptions of the different types of detecting methods with illustrative figures are given by Gordy, Smith and Trambarulo.[4]

Mercury Dimethyl and Diethyl.—Figure 1 shows the electron-magnetic resonances obtained for $Hg(CH_3)_2$ and $Hg(C_2H_5)_2$ at 77°K. after irradiation for several hours with 40 kv. X-rays. That for $Hg(CH_3)_2$ has a symmetric 5-line hyperfine structure with the intensity ratios and equivalent component spacing expected for 4 hydrogen nuclei equally coupled to the electron spin.[5] The g factor for the center of the group is essentially that of the free electron spin. This indicates that the spin orbit coupling is broken down. The total spacing is 98 ± 5 gauss. Within the accuracy of the observation, the quintet is that recently observed for several other irradiated solids including alanine and ethyl alcohol. The similar quintet in these compounds has been ascribed to the radical $(C_2H_4)^+$ which, in the valence bond language, may be described as a resonant hybrid of the forms



with a migrating "one-electron bond."

The magnetic field used in these experiments is such as to produce the Paschen–Bach effect, *i.e.*, both the electron spin and nuclear spin vector process about the direction of the applied field. Under these circumstances a total nuclear splitting of 500 gauss would be expected if the odd electron were to remain all the time in a 1s orbital of H. This splitting is independent of orientation and arises from the non-vanishing density $(\psi_0\psi_0^*)$ of the s wave function at the nucleus. If, as seems probable, the direct dipole–dipole interactions are averaged out by motions of the radicals, the observed spread of 98 gauss would indicate that the odd electron remains

---

[1] This work has been supported by a contract with the Office of Ordnance Research, Department of the Army.

[2] W. Gordy, W. B. Ard and H. Shields, *Proc. Nat. Acad.*, **41**, 983 (1955).

[3] (a) W. Gordy, W. B. Ard and H. Shields, *ibid.*, **41**, 996 (1955); (b) W. B. Ard, H. Shields and W. Gordy, *J. Chem. Phys.*, **23**, 1727 (1955), and reports to be published later.

[4] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953.

[5] For a discussion of nuclear effects on paramagnetic resonance of organic radicals, see W. Gordy, Chapter II, in "Chemical Applications of Spectroscopy," edited by Weissberger and West, Interscience Publishers, New York, N. Y., 1956.