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 $\cdot CH_2OH$, 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.

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[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

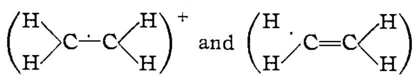
With microwave magnetic resonance of the unpaired electrons, we have studied the effects of ionizing X-rays on some simple organo-metallic compounds in the solid state. The results are in accord with the effects which might be anticipated from similar investigations recently made in this Laboratory on 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

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[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.

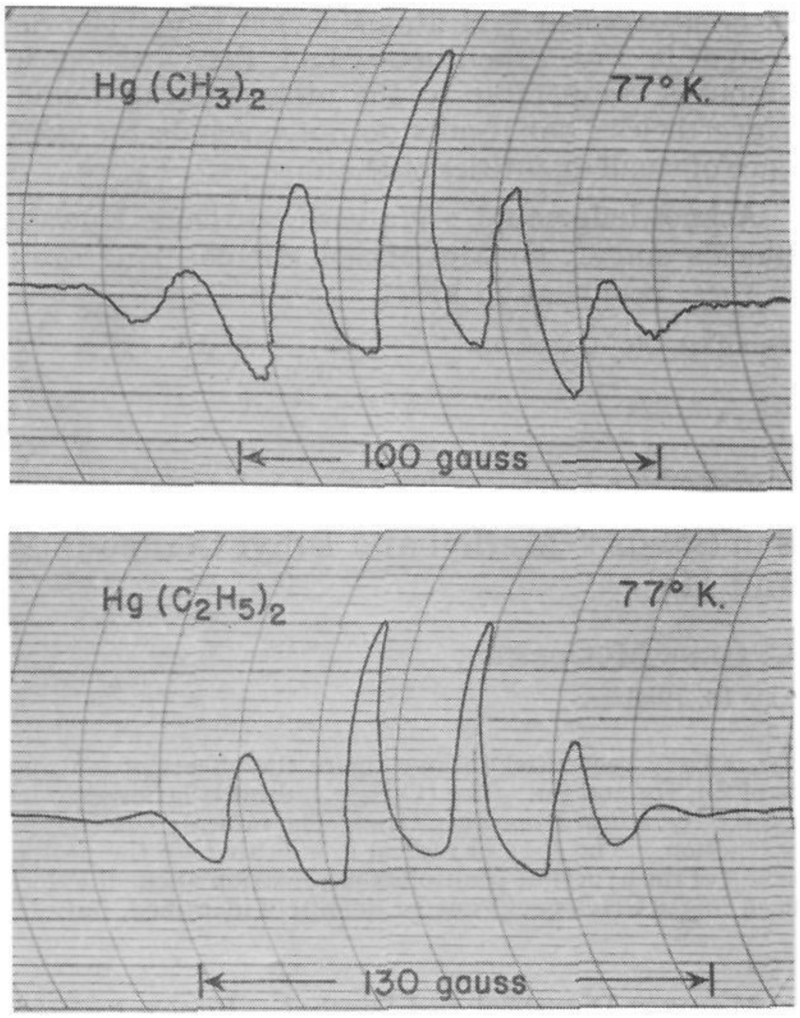

Fig. 1.—Electron spin resonances at 9 kMc. of X-irradiated mercury dimethyl and diethyl in the solid state. The tracings represent the second derivative of the actual absorption curve.

$^1/_5$ of the time in the 1s orbitals of the four hydrogens. The odd electron may then be regarded as in a molecular orbital formed as a linear combination of the atomic orbitals with the 1s atomic orbitals of each H contributing 5% and orbitals of the two carbons contributing the remaining 80%.

The pattern obtained for irradiated Hg(C_2H_5)$_2$ (Fig. 1) has six equally spaced components with the relative intensities (1, 5, 10, 10, 5, 1) expected for 5 protons equally coupled to the electron spin vector. This is indeed a surprising observation. It is not surprising that the ionization might here produce the ethyl free radical C_2H_5 which would have 5 protons coupled to the odd electron, but it is surprising that these 5 protons would be equally coupled to the spin vector of the odd electron. One would expect the coupling for protons of the CH_3 end to be different from those of the CH_2 end. Nevertheless, if the coupling of the CH_3 protons were significantly stronger than those of the CH_2 end, there would be 4 groups of three, or 12 components. If that of the CH_2 group were the stronger, there would be 3 groups of 4, or again 12 components. Only if the couplings to all five protons are equal, will there be just six components.

From the observed spread of 130 gauss we conclude that the odd electron of the tentative free ethyl radical remains in 1s orbitals of the five H atoms about 25% of the time. The simplest approach is to treat the odd electron as if it were in a molecular orbital to which the 1s wave functions of the five hydrogens each contribute 5% and the atomic functions of the two carbons contribute the remaining 75%. To account for the symmetrical sextet, one is tempted to think of the ethyl radical as a beautiful wheel with the five hydrogens symmetrically arranged in a plane and the carbons forming the hubs on either side. We have thus far been able to resist this temptation! The equivalent coupling might be explained by postulating a rapid exchange of protons between opposite ends of the ethyl radical, but we do not know from other sources whether such an exchange is probable or possible. Perhaps equivalent coupling is in some way achieved without proton exchange or molecular symmetry.

The clean resolution of the lines of Fig. 1 and the fact that the spacings of the lines for Hg(CH_3)$_2$ are the same as for irradiated alanine observed at room temperature indicate that these radicals are actually rotating or tumbling even at 77°K. If the radicals are fixed in space, they would be arbitrarily oriented in the polycrystalline sample and the direct dipole–dipole interaction of the unpaired electron (located mainly on the carbons) with the protons would seemingly smear out these structures into a broad, incompletely resolved pattern.[6] This evidence for tumbling or rotating motions suggests that the radicals are trapped in symmetrical cages. Such motions tend to average out or diminish internal field effects and direct dipole–dipole interactions sufficiently to cause certain radicals to have a similar recognizable pattern in a variety of solids. This is a fortunate circumstance which seems to be borne out by the large amount of data collected in our laboratory. A useful set of microwave "fingerprints" of radicals in solids is thus being accumulated. In most instances the motions of the radicals are probably of the restricted, barrier-tunneling variety, and often the anisotropic interaction terms may be only partly averaged out.

A tendency revealed indirectly by the data accumulated in our laboratory is for the ionized molecule of a solid to break up in such a way as to form the most stable combination of radicals and simpler molecules out of the broken pieces. In many instances this could not be achieved unless the broken pieces remained trapped for a time in the "cage" where the original molecule was broken up. Good evidence for this caging effect is provided by Hg(CH_3)$_2$. Certainly the radical (C_2H_4)$^+$ believed to be detected is not formed as a primary process of the X-irradiation. The most likely primary effect of the ionization is the production of CH_3 and ($HgCH_3$)$^+$. After the primary dissociation a series of reactions evidently follows in which the (C_2H_4)$^+$ is produced. The stable molecules which might be produced from the remaining pieces are Hg and H_2 or HgH_2. If a neighboring molecule is drawn into the reaction, two molecules of $HHgCH_3$ might be formed as an alternative. Under any circumstance the caging seems to be necessary. The radical (C_2H_4)$^+$ would hardly be produced by X-irradiation of gaseous Hg(CH_3)$_2$. In fact, it is difficult to see how it could be produced by irradiation of any gas except perhaps C_2H_4.

Unlike that for mercury dimethyl, the ethyl radi-

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[6] Such effects have been observed in our laboratory as similar radicals in certain other solids were stopped or severely restricted in their tumbling when cooled.

cal postulated in irradiated mercury diethyl could be produced as a primary effect of the ionization. The C_2H_5 would simply break off the ionized molecule to leave $(HgC_2H_5)^+$. Possibly the greater inertia of the two parts over those of mercury dimethyl prevents further reactions at 77°K.

Zinc Dimethyl.—Immediately after irradiation at 77°K. $Zn(CH_3)_2$ gave a quartet superimposed upon a weaker triplet, as shown in the upper curve of Fig. 2. Ten days later the quartet was found to have gone away, leaving the triplet, as is shown in the bottom curve of Fig. 3. We think the quartet may arise from the CH_3 radical, produced as a primary effect of ionization along with $(ZnCH_3)^+$. The CH_3 might later steal away an H atom from the $(ZnCH_3)^+$ to make methane and leave the radical $(ZnCH_2)^+$, which could give the triplet hyperfine structure from its two equally coupled hydrogens.

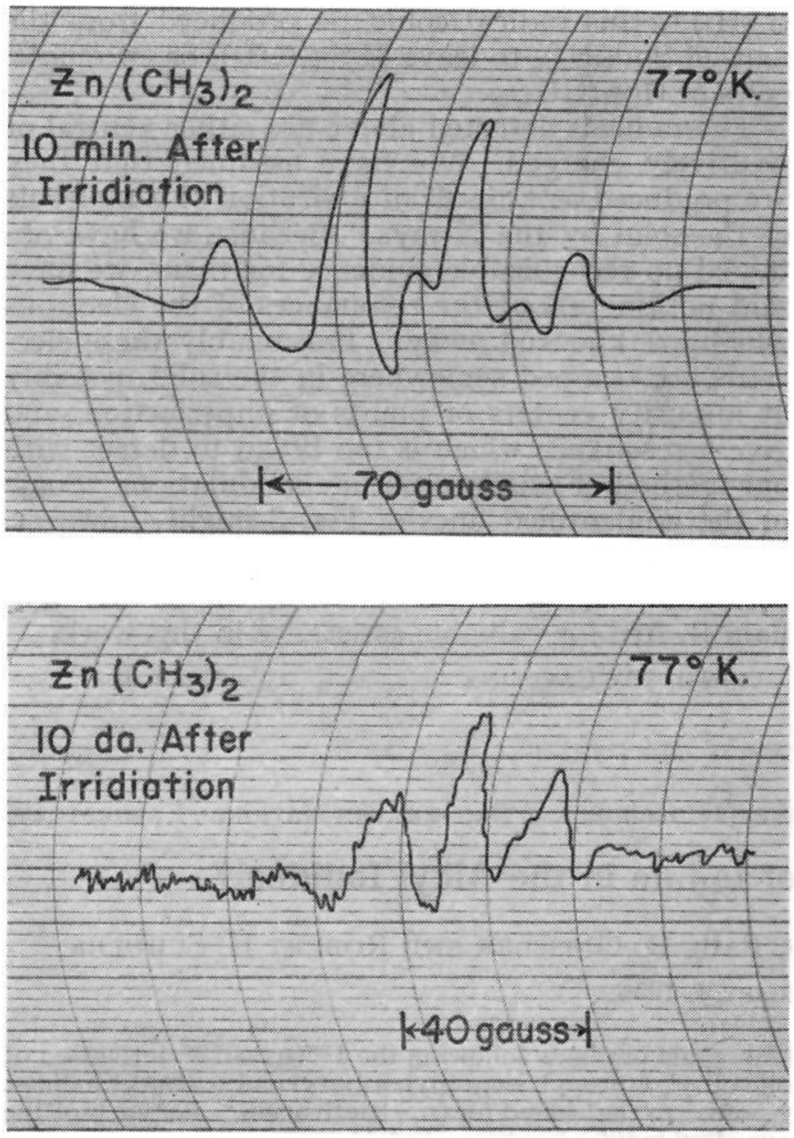


Fig. 2.—Electron spin resonance at 9 kMc. of X-irradiated zinc dimethyl in the solid state. The tracing represents the second derivative of the actual absorption curve.

The difference in the behavior of mercury dimethyl and zinc dimethyl is interesting. The electronegativity of Hg is 1.8, whereas that of Zn is only 1.5. It may be that this small difference, which favors the leaving of the positive charge on Zn, is mainly responsible for the difference in the way the two solids behave under ionizing radiations.

A quartet with approximately the same spacing as that observed for irradiated $Zn(CH_3)_2$ was earlier observed[3a] for irradiated palmitic acid at room temperature and for propionic acid at the temperature of liquid air. Since the same quartet has been here observed for irradiated $Zn(CH_3)_2$, it seems probable that the quartet with a total spread of 70 to 80 gauss is indeed the "fingerprint" of the methyl free radical. There seems to be no other radical likely to be produced in irradiated zinc dimethyl which could give the observed pattern.

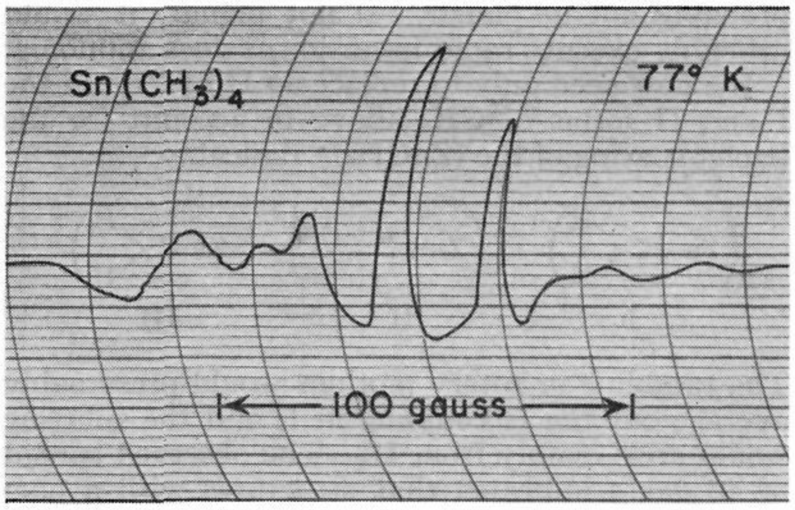
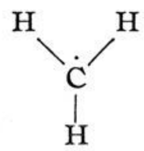


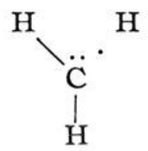
Fig. 3.—Electron spin resonance at 9 kMc. of tin tetramethyl in the solid state. The tracing represents the second derivative of the actual absorption curve.

Now that we believe the 75 gauss quartet likely arises from the methyl free radical, we are faced with the problem of accounting for the large splitting which is observed. We assume that it is due mainly to s occupancy of the H orbitals by the odd electron. The shape of the resonance indicates little direct dipole–dipole interaction. Furthermore, the odd electron must spend significant time in the 1s orbitals. Probable occupancy of the 2s orbitals of H could account for only a small fraction of the total splitting. The spread of 75 gauss then seems to require that the odd electron remain in the 1s orbitals of the H atoms a total of 75/500 of the time or again 5% of the time in the 1s orbital of each H. We seem required to assume that the CH bonds have "one-electron bond" contribution. The electronic structure of the CH_3 radical therefore might be regarded as a mixture of the forms



I

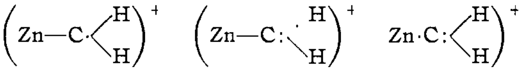
and



II

This strange situation in which a radical which seemingly could form three normal bonds actually forms on the average less than three may arise from the tendency of the 2s orbital of carbon to form a closed subshell with two paired electrons. If this tendency were to predominate, form II alone would represent the ground state of the radical, and a splitting of the order of 200 gauss should be observed. The observed splitting of 75 gauss indicates that form II contributes only about 40% to the ground state. In the actual structure, a compromise of the tendency to form a maximum number of covalent bonds and the tendency to fill the 2s shell of carbon is apparently reached with I contributing 60% and II, 40%. Since form II would probably employ three nearly pure p orbitals, the methyl free radical, if observed here, would probably not be planar. If not planar, it would probably execute rapid inversion as does ammonia.

We now need only to replace an H by Zn^+ in the I and II forms of CH_3 above to account for the triplet spacing of the $(ZnCH_2)^+$ radical.



I II III

The tumbling or rotary motions would presumably average out the H coupling in I, and the splitting would arise mainly from II. The observed spread of 40 gauss indicates that structures with a one-electron CH bond contribute about 20% to the ground state or that the odd electron remains 4% of the time in the 1s orbital of each H. Again the contributions from II might arise from the tendency of the C to fill its 2s subshell.

Tetramethyl Tin.—The paramagnetic resonance obtained for irradiated $Sn(CH_3)_4$ is incompletely resolved and more complex than those for the divalent Zn and Hg compounds. The pattern obtained, see Fig. 3, is almost certainly a superposition of the resonances of two or more radicals. It is possible that the two stronger lines with the first weak one to their right belong to the quintet of $(C_2H_4)^+$ and that the other two components on the left are made unrecognizable by unresolved lines of some unidentified radical. With the second derivative presentation, a resolved line has a maximum at the center with a minimum on either side. This shape leads to confusing and varied contours when two or more lines are incompletely resolved. However, we detected the $Sn(CH_3)_4$ with different amounts of modulation and also as a first derivative. The various curves obtained seem to bear out the interpretation that there is a strong quintet of about 95 gauss spread incompletely resolved from other lines. Nevertheless, this interpretation is by no means certain. If there is a quintet due to $(C_2H_4)^+$, this radical could be produced from the ionized $Sn(CH_3)_4$ to leave $H_2Sn(CH_3)_2$ or two molecules of $HSn(CH_3)_3$.

The radicals detected above are either neutral or positively charged. We have assumed that they are produced as a result of ionization of a molecule of the solid by the X-rays. Because we have obtained no recognizable evidence for them, we have said nothing about the resonances of the electrons which are knocked away. Presumably these electrons are trapped somewhere in the solid, possibly at impurity centers or points of imperfection, and give a resonance which is too broad to detect with our method of small amplitude modulation. Some of the unidentified lines of Fig. 3 might, however, result from F center resonances.

Acknowledgment.—We wish to thank Mr. William B. Ard for valuable assistance in this work.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, ST. PETER'S COLLEGE, AND BROOKHAVEN NATIONAL LABORATORY]

Chemical Effects of (n,2n) Activation of Iodine in the Alkyl Iodides[1,2]

BY CHARLES E. MCCAULEY, GEORGE J. HILSDORF, PAUL R. GEISSLER AND ROBERT H. SCHULER

RECEIVED FEBRUARY 4, 1956

The distribution of radioactive material between organic and inorganic products following the $I^{127}(n,2n)I^{126}$ activation of iodine by fast neutrons has been studied in both liquid and solid ethyl, *n*-propyl, isopropyl, *n*-butyl and *sec*-butyl iodides. The total organic retention has been found in all cases to be very similar to that found for (n,γ) activation. For each of the above materials, the distribution of I^{126} activity among the various alkyl iodides has been studied using carrier fractionation methods. In the case of ethyl iodide the product distribution observed for (n,2n) activation has been found to be very similar to that for (n,γ) activation. It is evident that the ultimate chemical fate of the radioactive nucleus is not dependent on the initial energy of the recoiling atom or on other variations which might be expected to result from the different nuclear processes. For all iodides, the activity is distributed among a number of components with the major fraction appearing in the parent material. The activity from solid *n*-propyl and *n*-butyl iodide is found to a considerable extent in the corresponding secondary iodide although in the case of the solid secondary iodides very little activity appears in the isomeric primary iodides. In general, products appear to be formed by reactions of the activated atom both in the epithermal region and, immediately after thermalization, with the radicals produced in the wake of the recoiling particle.

Previously it has been shown[3] that the retentions observed in the (d,p), (γ,n) and (n,2n) activation of iodine in methyl and ethyl iodide are nearly identical to those observed for (n,γ) activation.[4] The present work was undertaken in order to compare the retentions for the $I^{127}(n,\gamma)I^{128}$ and $I^{127}(n,2n)I^{126}$ processes in the solid alkyl iodides and to examine the distribution of activity among the various organic products resulting from the irradiation of both liquid and solid samples. More complete data on the values of the retention in the absence of scavenger iodine are also reported.

Levey and Willard[5] have measured the total organic retentions for the (n,γ) activation of eight lower alkyl iodides in both the liquid and solid phase and in the case of methyl and ethyl iodide have isolated the individual products using carrier fractionation techniques. In the present investigation, the use of the 13-day I^{126} activity produced by the fast neutron activation of the alkyl iodides makes it possible to carry out fractionation studies on more complex systems. Information on the distribution of

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minn., September 14, 1955.

[2] Research carried out in part under the auspices of the U. S. Atomic Energy Commission.

[3] R. H. Schuler, *J. Chem. Phys.*, **22**, 2026 (1954).

[4] The conventional term "retention" is used throughout this paper to describe the fraction of activity which appears in organic combination. The "retained" activity results from the reformation of organic species and not from non-rupture of the original bonds.

[5] G. Levey and J. E. Willard, THIS JOURNAL, **75**, 6161 (1953).