$$\langle \psi_p(i) | T(i) + U_p^+(i) | \psi_p(i) \rangle = -11.92 + 2.24 \text{ e.v.} = -9.68 \text{ e.v.}$$

The interesting thing to note here is that the experimental ionization potential of methyl radical is 9.80 e.v.,[41] a difference of only 0.12 e.v. from the integral shown above.

What this simplified calculation suggests is that the quantity $\langle \chi_p(i) | T(i) + U_p^+(i) | \chi_p(i) \rangle$ should be identified with the experimental ionization potential of the methyl radical!

No detailed discussion has been made of the computer programs used here. Such SCF programs are becoming commonplace in many laboratories, the program of each laboratory being unique in detail only. We, therefore, felt that a description of our programs was unnecessary. A possible unique feature of our program is the way in which the core elements H_{pq}^λ and H_{pp}^λ are automatically calculated. Details of the program can be obtained from the authors.

Acknowledgment. The authors gratefully acknowledge the suggestions and encouragement of Professor P. G. Lykos. R. L. M. wishes to acknowledge the support of National Institute of Health Grant GM 10826-01.

Appendix

In the description of the method in the Selection of Parameters section, it was mentioned that off-diagonal elements H_{pq}^λ for nonnearest neighbors are set equal to zero before forming the Fock matrix. Table X shows the values of these integrals for two typical examples, illustrating that the integrals are in fact small and can be set equal to zero with essentially no effect on the final result.

(41) C. E. Melton and W. H. Hamill, *J. Chem. Phys.*, 41, 2948 (1964).

Electron Spin Resonance Spectra of γ-Irradiated Polycrystalline Alkyl Iodides[1,2]

Harold W. Fenrick and John E. Willard

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. *Received September 13, 1965*

Abstract: It has been previously shown[3] that polycrystalline C_2H_5I which has been γ-irradiated at 77°K gives an unexpectedly complex esr spectrum with more than 32 lines spread over 1000 gauss. Similar complexity with varying spreads was found for the polycrystalline forms of other normal alkyl iodides having an even number of carbon atoms per molecule, but not for the odd-carbon-number species or for the glassy forms. To assist in determining the cause of the complex signals, spectra have been taken of C_2H_5I prepared from I^{129}, rather than the naturally occurring I^{127}, and of C_2D_5I, to learn whether changes in the spins and nuclear magnetic moments of the iodine and hydrogen atoms affect the pattern. The spectrum of the polycrystalline $C_2H_5I^{129}$ is indistinguishable from that of $C_2H_5I^{127}$, while that of $C_2D_5I^{127}$ has the wide spread of the latter, but fewer and broader lines. These data are interpreted to indicate that the breadth of the spectra results from coupling of the spin of the unpaired electron with orbital angular momentum on the iodine to give radicals with anisotropic apparent g values ranging from about 1.7 to 2.3. The many lines are the result of superposition of the hydrogen hyperfine splitting spectra of radicals oriented to give different apparent g values. Similar complex spectra are produced in $(C_2H_5)_3SnI$ (1000 gauss) and CH_2I_2 (700 gauss). Momentary warming from 77° to a temperature slightly under the melting point, followed by return to 77°, causes the complex spectra of C_2H_5I and i-C_3H_7I to decrease while a simpler spectrum grows. This occurs only in those samples which are frozen to the polycrystalline form following supercooling and not in those frozen slowly from a seed crystal, suggesting that a dissociative neutralization process may be favored by release of strain energy.

We have reported earlier[3] that n-alkyl iodides containing an even number of carbon atoms per molecule give esr spectra with an unexpectedly widespread and large number of lines following γ-irradiation in the polycrystalline state at 77°K. The purpose of the present work has been to seek an explanation of these complex spectra utilizing isotopic substitution, orientation effects, annealing studies, and radiolyses of related systems as sources of information.

Experimental Section

C_2D_5I of stated isotopic purity of $\geq 99\%$ was obtained from Merck Sharp and Dohme Ltd. It was used both as received and after passage through a preparative gas chromatography column. The results were the same for both types of sample. $C_2H_5I^{129}$ was synthesized by the reaction $(C_2H_5)_4Sn + I_2{}^{129} \rightarrow (C_2H_5)_3SnI^{129} + C_2H_5I^{129}$, in the manner used by Iyer and Martin[4] for the synthesis of $C_3H_7I^{129}$. Research grade tetraethyltin obtained from Peninsular Chemresearch and $I_2{}^{129}$ from the Oak Ridge National

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(1) This work was supported in part by the U. S. Atomic Energy Commission (Contract AT(11-1)-32) and by the W. F. Vilas Trust of the University of Wisconsin. We are indebted to Professor R. N. Dexter of the University of Wisconsin Physics Department for substantial assistance in use of the esr equipment.

(2) Further details of this work are given in the Ph.D. thesis of H. W. Fenrick, University of Wisconsin, 1966, available from University Microfilms, Ann Arbor, Mich.

(3) H. W. Fenrick, S. V. Filseth, A. L. Hanson, and J. E. Willard, *J. Am. Chem. Soc.*, 85, 3731 (1963).

(4) R. M. Iyer and G. R. Martin in "Proceedings of the 1960 Prague Symposium on Chemical Effects of Nuclear Transformations," Vol. I, International Atomic Energy Agency, Vienna, 1961 p 283.

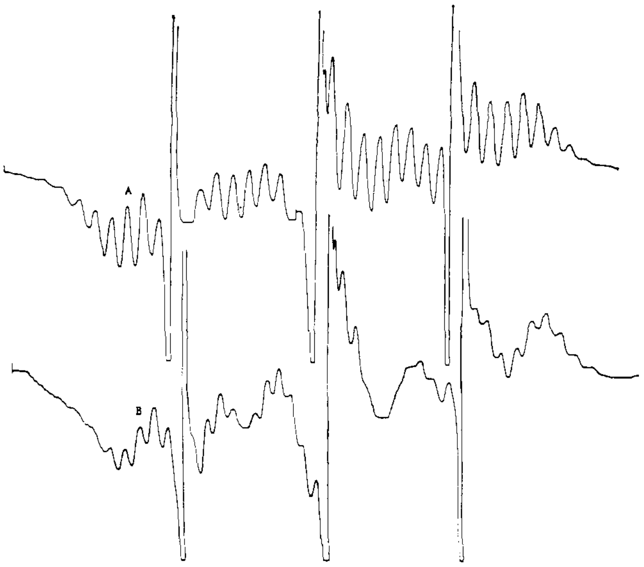

Figure 1. Esr spectrum of γ-irradiated polycrystalline $C_2H_5I^{129}$, shown at two orientations differing by 90°: dose, 5×10^{19} ev g^{-1}; 77°K;[7] signal level, 160.

Laboratory were mixed in equimolar amounts and allowed to stand in normal room light[5] for 1 hr. Activation analysis indicated that the I_2^{129} contained less than 3% I^{127}.[6] The ethyl iodide was distilled on the vacuum line through activated alumina and condensed in the Suprasil sample tube used for esr measurements. Use of the alumina was necessary to remove the triethyltin iodide completely. Amounts of $(CH_3)_3SnI$ of considerably less than 1% gave an esr signal superimposed on that of polycrystalline C_2H_5I. The yield of $C_2H_5I^{129}$ was 90% of theoretical. Triethyltin iodide for γ-irradiation and esr examination was obtained as a by-product of the $C_2H_5I^{129}$ preparation. It was freed of C_2H_5I by removing all material volatile at room temperature to a trap at 77°K on the vacuum line. The I^{129} incorporated in the triethyltin iodide could be recovered by hydrolyzing with alcoholic KOH, precipitating as PdI_2 by adding $PdCl_2$, and heating to liberate iodine from the PdI_2. Other methods tested[2] for the synthesis of $C_2H_5I^{129}$ and found less satisfactory included refluxing of C_2H_5OH, I_2, and P_4 together, refluxing of C_2H_5OH-HI mixtures, and illumination of C_2H_4-HI-I_2 mixtures.

Eastman White Label C_2H_5I and i-C_3H_7I were used without further purification, since fractional distillation and passage through activated alumina or purification by gas chromatography produced no differences in the esr spectra found after γ-irradiation at 77°K. All samples for irradiation and esr examination were degassed and dried with P_2O_5 on the vacuum line and sealed under vacuum.

γ-Irradiations were made in liquid nitrogen at dose rates of about 3×10^{18} ev g^{-1} min^{-1} for 20 min, using a Co^{60} source.

Esr spectra were determined with a Varian Associates V-4500 spectrometer, using 100-kc modulation. Samples were examined at 77°K while under liquid nitrogen. A modulation amplitude setting of 1250 (about 4 gauss), a power level attenuation of 10 decibels, a scanning rate of about 100 gauss/min, and a chart speed of 1 in./min were used in most of the work. The direction of scan was always with magnetic field increasing from left to right in the figures. Radical detection sensitivity increased nearly linearly with an increase in the signal level settings recorded on the figures of this paper. The spectral widths are indicated by the 507-gauss separation of the H doublet lines from the Suprasil sample tubes.

Glassy samples of the alkyl iodides are usually most readily prepared by immersing the esr tube containing the liquid into liquid nitrogen up to the height of the liquid for a moment and then immersing farther. Polycrystalline samples of ethyl iodide were usually prepared from the glassy form by warming it to a temperature slightly below its melting point, at which temperature spontaneous crystallization occurs. Polycrystalline samples also form after slowly supercooling the liquid to temperatures 5 to 15° below the melting point. Polycrystalline samples of the same alkyl iodide frozen by these two methods gave identical esr spectra.

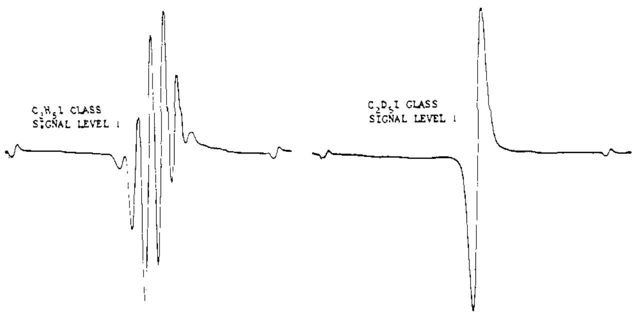

Figure 2. Esr spectra of γ-irradiated glassy C_2H_5I and C_2D_5I: dose, 7×10^{19} ev g^{-1}; 77°K.

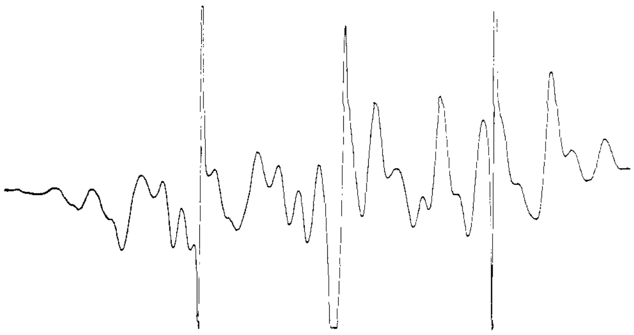

Figure 3. Esr spectrum of γ-irradiated polycrystalline C_2D_5I: dose, 7×10^{19} ev g^{-1}; 77°K;[7] signal level, 200.

Results

Comparison of $C_2H_5I^{129}$ with $C_2H_5I^{127}$. Figure 1 shows two esr spectra taken on the same sample of γ-irradiated polycrystalline $C_2H_5I^{129}$ at 77°K. These are essentially identical in total spread (*ca.* 1000 gauss) and number of lines[7] (more than 30) with the spectra obtained[3,8] at appropriate orientation of similar $C_2H_5I^{127}$ samples, despite the fact that the nuclear spin of I^{129} is $^7/_2$ and that of I^{127} is $^5/_2$. They are in contrast to the six-line ethyl radical spectrum shown by glassy C_2H_5I samples[3] (Figure 2). The spectrum obtained from $C_2H_5I^{129}$ glass is identical with that from $C_2H_5I^{127}$ glass.

Comparison of C_2D_5I with C_2H_5I. The spectrum from polycrystalline C_2D_5I (Figure 3) has a spread similar to that of C_2H_5I (Figure 1) but has fewer and broader lines. Glassy samples of C_2D_5I give a single-line spectrum approximately 50 gauss wide (Figure 2) in contrast with the six-line spectrum of *ca.* 160 gauss of C_2H_5I. The broad single line is probably the envelope of the individual lines in the C_2D_5 spectrum, the narrowing of the total spectrum relative to that of C_2H_5 resulting from the fact that the magnetic moment of the deuterium nucleus is smaller by a factor of 3.25 than that of the protium nucleus.

Orientation Effects. The spectra of both C_2H_5I and C_2D_5I in the polycrystalline state showed changes

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[5] Earlier tests have shown that no reaction occurs between tetrapropyl tin and iodine in 24 hr in the dark: R. M. Iyer, private communication.

[6] D. D. Wilkey and J. E. Willard, *J. Chem. Phys.*, in press.

[7] The two intense lines at the right and left of the spectra are the hydrogen doublet resulting from H atoms produced in the Suprasil sample tube. The separation between these lines is 507 gauss. The two relatively intense, poorly resolved lines in the center of the spectra are also observed in γ-irradiated empty Suprasil tubes at 77°K.[3]

[8] G. L. Hermann, M.S. Thesis, Air Force Institute of Technology, Wright Patterson Air Force Base, Ohio, July 1965.

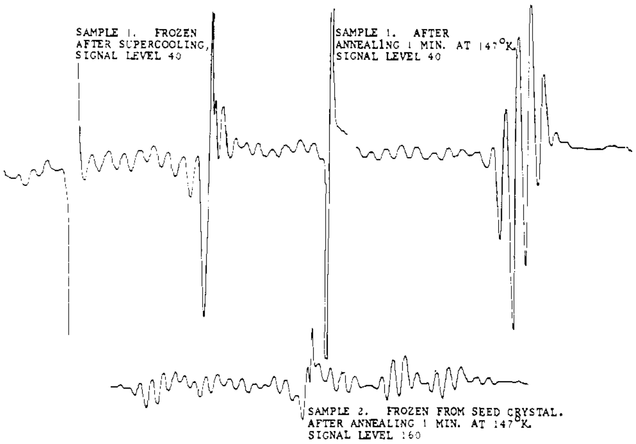

Figure 4. "Momentary anneal" effects on esr spectra of two samples of γ-irradiated polycrystalline ethyl iodide, frozen by different procedures: dose, 6×10^{19} ev g^{-1}; 77°K.[7]

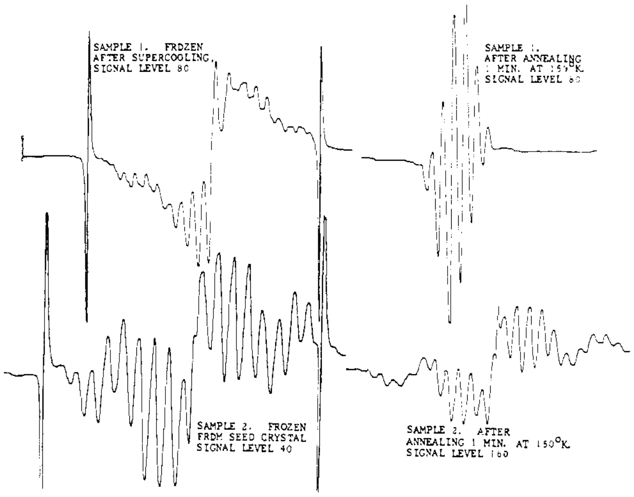

Figure 5. "Momentary anneal" effects on esr spectra of two samples of γ-irradiated polycrystalline isopropyl iodide, frozen by different procedures: dose, 6×10^{19} ev g^{-1}; 77°K.[7]

in the relative intensities of individual lines when the sample was changed from one position to another by rotating around the vertical axis of the sample tube in 45° increments, as illustrated in Figure 1. The total width of the spectrum did not change. Spectra for positions which differed by 180° were identical.

The magnitude of the orientation effect was independent of the rate at which the sample was frozen; a sample frozen very slowly from a seed to give large segments which were transparent gave essentially the same spectrum and changes with orientation as a rapidly formed polycrystalline mass.

Orientation tests with polycrystalline samples of i-C_3H_7I, n-C_4H_9I, n-$C_6H_{13}I$, and n-$C_8H_{17}I$, all of which give complex spectra with similarities to that of ethyl iodide, did not show any changes in the spectra with orientation. The spectra of alkyl halide glasses did not change with change of orientation.

"Momentary Anneal" Effect. In the course of these studies, the esr spectrum of a sample of γ-irradiated polycrystalline C_2H_5I was observed at 77°K, following which the sample was placed in the Varian variable-temperature device at 145–150°K for 1 min and then returned to 77°K for further esr examination. The treatment produced a small decay of the complex polycrystalline C_2H_5I pattern, accompanied by the appearance of a stronger central six-line, 160-gauss C_2H_5 radical pattern of the type observed in glassy samples. This, and the similar behavior of polycrystalline i-C_3H_7I samples which produce an isopropyl radical-type spectrum after momentary anneal, are illustrated in Figures 4 and 5. The melting points are: C_2H_5I, 165°K; i-C_3H_7I, 182°K. Two features of the central six- and eight-line spectra produced by the momentary anneal of these compounds are notable: (1) there is no evidence of these signals when identical samples are slowly warmed from 77°K to the melting point; (2) the C_2H_5 signal produced in this way in polycrystalline C_2H_5I decays only slowly at temperatures up to nearly 140°K, whereas the similar signal produced by irradiation of glassy samples decays rapidly at 100°K.

Equally as surprising as the occurrence of the momentary anneal behavior was the discovery that the production of the simpler spectrum occurs only with samples supercooled before crystallization and not in those frozen slowly from a seed crystal. For the latter, the momentary anneal results in decrease of the original pattern without qualitative change. The supercooling may consist either of freezing the sample to a glass (in the case of C_2H_5I) and crystallizing by warming, or in slowly supercooling below the melting point until freezing occurs. Isopropyl iodide always crystallizes rather than forming a glass when the sample is plunged into liquid nitrogen. Samples prepared in this way gave the same results as those prepared by slow crystallization from a seed crystal. It is noteworthy that i-C_3H_7I supercooled before freezing gives a significantly different spectrum than a sample frozen slowly from a seed.

An attempt was made to observe slow growth of the six-line C_2H_5 radical spectrum from the 32-line spectrum of polycrystalline C_2H_5I, in the 140–150°K temperature range. At 140°K the 32-line spectrum decreased in intensity with no change in the relative intensity of the lines. Another sample was transferred to the Varian variable temperature device in the esr cavity at 145°. By the time the central portion of the spectrum could be scanned, the six-line pattern had grown to its maximum intensity. When a second scan was taken 5 min later, this intensity had dropped to half its maximum, while in the same period the complex spectrum on the wings decreased to about one-fourth.

Six other polycrystalline alkyl iodides studied differed from the ethyl and isopropyl in that they showed significant qualitative spectral changes when slowly warmed.[2]

Spectra of γ-Irradiated $(C_2H_5)_3SnI$ and CH_2I_2. γ-Irradiated $(C_2H_5)_3SnI$ glass at 77°K gave a six-line esr signal identical with that of C_2H_5I glass. The polycrystalline form of the tin iodide gave the 1000-gauss spectrum shown in Figure 6, while a polycrystalline sample of $(C_2H_5)_4Sn$ gave a five-line pattern 200 gauss wide. Thus, the substitution of an iodine atom for an ethyl group changes the spread of the esr spectrum from 200 to 1000 gauss.

Polycrystalline CH_2I_2 required longer irradiation than the other alkyl iodides to produce a satisfactory esr signal. After a 3-hr irradiation, an asymmetric signal of about 700 gauss with structure extending beyond the hydrogen doublet lines on both sides was obtained. The lines were broad, only about 10 peaks and shoulders being resolvable. They decayed by less than a factor of 5 in 3 months at 77 °K.

Discussion

Explanation of Spectral Widths of Polycrystalline Samples. The detailed similarity between the esr spectra of γ-irradiated polycrystalline $C_2H_5I^{129}$ and $C_2H_5I^{127}$ establishes the fact that the unusual breadth of these spectra is not caused by hyperfine splitting due to coupling of the unpaired electron with iodine. If such coupling were responsible, the $C_2H_5I^{129}$ would show $^4/_3$ as many lines as $C_2H_5I^{127}$, because the nuclear spin of I^{129} is $^7/_2$, while that of I^{127} is $^5/_2$. Hyperfine splitting by hydrogen is ruled out as the cause of the 1000-gauss spread, because the splitting by free H atoms is known to be only 507 gauss and also because the spectrum of C_2D_5I is as wide as that of C_2H_5I. Hyperfine splitting by deuterium yields a smaller spread than that by protium because of its lower nuclear magnetic moment (0.86, as compared to 2.92 nuclear magnetons), as illustrated in Figure 2.

On the basis of the above considerations, the large spread must be caused by an interaction of the unpaired electron other than with the nuclear spins. This interaction must involve iodine, since such broadened spectra are not observed in any pure hydrocarbons, but are found for all of the even-carbon-number normal alkyl iodides tested and also for i-C_3H_7I, $(C_2H_5)_3SnI$, and CH_2I_2. Nuclear quadrupole effects, which can produce broadening, can be ruled out on the basis of the equal spreads of the I^{129} and I^{127} ethyl iodide spectra. Spin–spin interaction, which is sometimes responsible for large splittings, is not applicable to the system and the spectra under consideration here. A spin–orbit interaction, however, offers a plausible explanation of the broad spread of the spectra. If the unpaired electron is somewhat localized on a p orbital of an iodine atom in its radical, this would result in a large amount of coupling between the spin angular momentum of the electron and its orbital angular momentum.

The magnitude of spin–orbit interaction depends on:[9] (1) the number and configuration of the outer electrons; (2) the value of the orbital angular momentum and the spin angular momentum for the term involved; (3) the atomic number of the atom on which the electron is localized (the spin–orbit interaction increases approximately in proportion to the cube of the atomic number).

The spin–orbit interaction may be expressed as an anisotropic coupling between the electron spin and the external magnetic field.[9] This makes it easier to reorient the spin in some directions of the field than in others. A radical in an orientation such that the orbital angular momentum makes the electron spin reorient more easily will undergo resonance at a lower magnetic field than if the orbital angular momentum were not present. This situation may be described by assigning the radical in this orientation a larger g factor than would be assigned if there were zero orbital angular momentum interaction. Conversely, a radical oriented such that the orbital angular momentum makes the electron spin more difficult to reorient will undergo resonance corresponding to a higher g factor. As has been discussed,[10] the esr spectrum of a polycrystalline sample is due to the superposition of the spectra corresponding to radicals in various orientations, *i.e.*, radicals with various g factors. A variation in g factor from 1.7 to 2.3 would be required to obtain the spread of 1000 gauss centered at the free electron resonance of 3300 gauss observed in the polycrystalline C_2H_5I spectrum. In transition metal compounds where spin–orbit coupling is pronounced, anisotropic g values sometimes differ by a factor of 10.

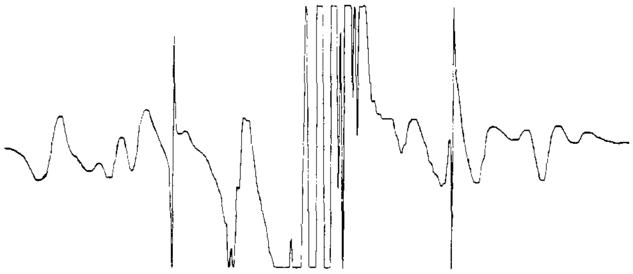

Figure 6. Esr spectrum of γ-irradiated polycrystalline $(C_2H_5)_3SnI$: dose, 6 × 10^{19} ev g^{-1}; 77°K;[7] signal level, 40.

If spin–orbit coupling is responsible for the breadth of iodide spectra such as those of Figures 1 and 3, it might be expected that the iodine would also contribute to the hyperfine splitting. This splitting may be unresolved, as are the 18 lines of the hyperfine splitting spectrum of atomic iodine which can be readily observed in the gas phase,[11a] but is not seen in solid matrices.[11b]

The 700-gauss spread given by polycrystalline n-butyl iodide, the 500-gauss pattern from isopropyl iodide, the 350-gauss patterns from n-hexyl and n-octyl iodides,[3] and the structure on the low-field side of the central six-line pattern from γ-irradiated ethyl iodide glass when observed at high sensitivity[3] may result from weaker spin–orbit interactions than that which occurs in polycrystalline ethyl iodide. Mitchell, Green, and Spinks[12] have suggested that the low-field structure observed in γ-irradiated polycrystalline ethyl bromide[3,12,13] is due to a bromine-containing radical in which spin–orbit coupling with the bromine is significant. Low-field structure asymmetric with respect to the free-electron g value has also been observed[3,14] for γ-irradiated polycrystalline and glassy n-C_4H_9Br and in glassy n-C_4H_9Br containing 7 mole % Br_2. In the glassy samples, 15 or more poorly resolved lines in addition to the usual[3,13] six-line $RCH_2CH_2\cdot$ spectrum are observable, extending between $g = 1.85$ and 2.25.[3,14]

Multi-Line Character of Polycrystalline Samples. If the 1000-gauss spread of the spectra of Figures 1, 3, and 4 is caused by spin–orbit coupling, giving a series

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(9) A. Carrington and H. C. Longuet-Higgins, *Quart. Rev.* (London), **14**, 427 (1960).

(10) R. Lefebvre, *J. Chem. Phys.*, **33**, 1826 (1960).

(11) (a) S. Aditya and J. E. Willard, *ibid.*, in press; (b) *J. Am. Chem. Soc.*, **88**, 229 (1966).

(12) F. W. Mitchell, B. C. Green, and J. W. T. Spinks, *J. Chem. Phys.*, **36**, 1095 (1962).

(13) P. B. Ayscough and C. Thompson, *Trans. Faraday Soc.*, **59**, 1477 (1962).

(14) R. M. A. Hahne and J. E. Willard, *J. Phys. Chem.*, **68**, 2582 (1964).

of anisotropic apparent *g* values, it seems probable that the large number of lines is the result of the superposition of the hydrogen hyperfine splitting spectra of radicals oriented to give different apparent *g* values. The presence of fewer and broader lines in the spectrum of C_2D_5I than in that of C_2H_5I (Figures 1 and 3) proves that the lines are the result of hyperfine splitting by the hydrogen atoms and is consistent with the effect of deuterium substitution on the simpler ethyl radical spectrum in the glass shown in Figure 2.

Species Responsible for Spectra. Thus far in the discussion the broad spectra have been attributed to spin–orbit coupling with iodine without considering the chemical identity of the species responsible. Iodine species having an unpaired electron which may be present in the γ-irradiated matrices giving these spectra include I, I_2^-, RCHI, RI^+, and RI^-. The first two of these seem to be eliminated by the isotopic substitution results which show that the observed line structure is caused by hyperfine splitting by hydrogen atoms.

One interpretation of the "momentary anneal" effects shown in Figures 4 and 5 is that a process is able to occur at the anneal temperature which converts the species responsible for the complex spectrum to that responsible for the simpler central spectrum. In the case of the polycrystalline ethyl iodide, such a process might be $C_2H_5I^+ + I^-$ (or $C_2H_5I^-$) $\rightarrow C_2H_5$ (or $2C_2H_5$) $+ I_2$, with $C_2H_5I^+$ or $C_2H_5I^-$ being responsible for the broad spectrum. The fact that the "momentary anneal" effect occurs only with crystals frozen after supercooling and does not occur with crystals frozen slowly from a seed, or with those allowed to stand for several days prior to irradiation following freezing, suggests that it is aided by a release of strain energy or change of crystal state that occurs sharply in the narrow temperature range observed for momentary anneal.

It seems more probable that $C_2H_5I^+$ or $C_2H_5I^-$, rather than C_2H_4I, is responsible for the broad spectrum, because the latter offers less possibility for conversion to C_2H_5 during momentary anneal. Esr examination of systems in which C_2H_4I might be formed by the reactions $C_2H_4 + I \rightarrow C_2H_4I$ or $C_2H_3I + H \rightarrow C_2H_4I$, using H and I atoms formed by the photolysis of HI, has shown no evidence of the broad spectra.[11b]

It is probable that the same types of trapped intermediates are formed in the alkyl iodide glasses and in the polycrystalline samples with odd carbon number as in the polycrystalline samples with even carbon number. Thus it appears that a determining factor as to whether a given trapped species produces the broad spectrum is the nature of the crystal lattice in which it resides.

An Electron Diffraction Study of Trimethylsilyl Isothiocyanate and Trimethylsilyl Isocyanate

K. Kimura, K. Katada, and S. H. Bauer

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. *Received August 25, 1965*

Abstract: The molecular structures of $(CH_3)_3SiNCS$ and $(CH_3)_3SiNCO$ in the gaseous state were determined by electron diffraction using sector–microphotometer data. Neither species was found to have C_{3v} symmetry. The bond distances as observed (center of gravity parameter, r_g) and the bond angles are as follows. For $(CH_3)_3SiNCS$ $r_g(C—H) = 1.09 \pm 0.02$, $r_g(C{=}S) = 1.56 \pm 0.01$, $r_g(N{=}C) = 1.18 \pm 0.01$, $r_g(Si—N) = 1.78 \pm 0.02$, $r_g(C—Si) = 1.87 \pm 0.01$ A, and $\angle(Si–N–C) = 154 \pm 2°$. For $(CH_3)_3SiNCO$ $r_g(C—H) = 1.10 \pm 0.02$, $r_g(C{=}O) = 1.18 \pm 0.01$, $r_g(N{=}C) = 1.20 \pm 0.01$, $r_g(Si—N) = 1.76 \pm 0.02$, $r_g(C—Si) = 1.89 \pm 0.01$ A, and $\angle(Si–N–C) = 150 \pm 3°$.

Microwave and electron diffraction studies of isocyanates and isothiocyanates have indicated that these molecules do not possess axial symmetry: the valence angles at the nitrogen atom are $128.1 \pm 0.5°$ for HNCO,[1] $130.25 \pm 0.25°$ for HNCS,[2] $132.25 \pm 0.25°$ for DNCS,[2] $125 \pm 5°$ for H_3CNCO,[3] and 142° for H_3CNCS.[4] The more recent microwave studies of H_3CNCS,[5] H_3CNCO,[6] H_3CNSO,[7] and H_3CNCH_2[8] also have shown the presence of internal rotation about a single threefold axis, wherein the barriers to internal rotation of the CH_3 groups are low in both H_3CNCS and H_3CNSO, intermediate in H_3CNSO, and quite high in H_3CNCH_2.

The silanes appear to be different. The infrared and Raman spectra[9] and the microwave spectra[10] of H_3SiNCS and of its deuterated compounds led to the conclusion that these species belong to the symmetry class C_{3v}, with the heavy atoms in linear array. Also,

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(1) L. H. Jones, J. N. Shoolery, R. G. Shulman, and D. M. Yost, *J. Chem. Phys.*, **18**, 990 (1950); also studied by electron diffraction by E. H. Eyster, R. H. Gillette, and L. O. Brockway, *J. Am. Chem. Soc.*, **62**, 3236 (1940); and by infrared spectroscopy by C. Reid, *J. Chem. Phys.*, **18**, 1544 (1950).

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(3) E. H. Eyster, R. H. Gillette, and L. O. Brockway, *J. Am. Chem. Soc.*, **62**, 3236 (1940).

(4) C. I. Beard and B. P. Dailey, *ibid.*, **71**, 929 (1949).

(5) S. Siegel, Thesis, Harvard University, 1958.

(6) R. F. Curl, Jr., V. M. Rao, K. V. L. N. Sastry, and J. A. Hodgeson, *J. Chem. Phys.*, **39**, 3335 (1963).

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