viscosity, which is one reason why calculated values of τ turn out too large when one uses η_l or η_m in the Debye equation.

The three different methods of calculating the dipole moment show excellent agreement for adamantane chloride and a small discrepancy between the Debye method and the other two for the bromide. The discrepancy is no larger than that frequently observed.[14] The dipole moments of adamantane chloride and adamantane bromide calculated with the use of the refraction for the D-line are considerably larger than all of the values previously reported[21] for alicyclic and ali-

phatic halides. When, however, values of the total induced polarization (electronic polarization + atomic polarization) estimated from a_∞ are used in the moment calculation, instead of the molar refraction for the sodium D line, the moment values obtained are close to those found for the branched-chain and cyclic chlorides and bromides, e.g., t-butyl chloride, 2.13; t-butyl bromide, 2.17; cyclopentyl bromide, 2.20; cyclohexyl chloride, 2.2; and cyclohexyl bromide, 2.2. These are slightly higher than the values found for the smaller chlorides and bromides, probably, because of inductive effects. The moment values for the two adamantane compounds are, therefore, what would be expected, but the reason for their high atomic polarization values is not apparent.

(21) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 269, 274.

Formation and Identification of Unique Radical Sites in Irradiated Amides

BY E. J. BURRELL, JR.

The free radicals produced in each of ten N-substituted amides by irradiation with 2-Mev. electrons have been characterized by their e.p.r. spectra. A single species of radical is formed in each of nine of the amides. The G(radical) yield for N-(n-propyl)-propionamide is 4.7 ± 1.4.

Introduction

Electron paramagnetic resonance (e.p.r.) spectroscopy can be a powerful tool in the characterization of free radical intermediates formed in radiation reactions. Because the concentration of these radicals is so low and their lifetimes so short, it has been necessary, in the first phase of such a characterization program, to accumulate the otherwise transient species in a frozen matrix. Although this accumulation of frozen free radicals gives rise to a strong e.p.r. signal, the observed e.p.r. spectrum may be influenced by the very matrix which stabilizes the radicals.[1]

In some environments, however, the perturbation of the radical spectrum by the crystal lattice is small and the e.p.r. spectrum represents in a simple way the chemical structure of the radical. Ten members of the class of N-substituted amides, presented here, have e.p.r. spectra which characterize the radicals present. Three members of the class of quaternary ammonium halides previously discussed also show this behavior.[2] The e.p.r. spectrum of a single kind of radical formed in an irradiated solid has been observed in a number of other cases.[3-6]

Care must be taken that any anisotropic dipolar interaction of the unpaired electron be considered.[7]

It will be seen from the correlation of e.p.r. spectra with radical structure in examples reported here that anisotropic effects do not appear to interfere with the identification of the free radical structure.

Experimental

The N-substituted amides were synthesized for this study by members of the Carothers Laboratory, Textile Fibers Dept., E. I. du Pont de Nemours & Co. The fact that only one kind of radical is formed in nine of the amides is taken as a sufficient indication of purity. Two kinds of radicals appear in the other amide and probably represent two modes of decomposition rather than an impurity. Nuclear magnetic resonance analysis was used to confirm the molecular structure of each amide before irradiation.

Each amide was evacuated and sealed off at 10^{-5} mm. in a "Thermosil" (available from Thermal American Fused Quartz Co., Dover, New Jersey) quartz tube and irradiated at -80 or $-195°$ with 2-Mev. electrons from the General Electric Resonant Transformer in this Laboratory. Neither color centers nor an e.p.r. signal was observed in the irradiated "Thermosil" quartz tube itself.

The e.p.r. spectra were obtained using a modified Varian V-4500 spectrometer.[8] A quartz Dewar in the cylindrical e.p.r. cavity held the sample tube at $-80°$ or $-195°$.

Computation of Predicted E.P.R. Spectra.—An I.B.M. 650 digital computer was programmed to compute the differential e.p.r. spectrum to be expected for a given model of the environment of the unpaired electron. The computer adjusted the hyperfine splitting and line-width parameters so as to give a least squares fit between the computed spectrum and the experimental spectrum. The computed e.p.r. spectra are shown in the figures with the corresponding experimental spectra. The detailed programming and computational techniques will appear shortly.

(1) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Academic Press, Inc., New York, N. Y., 1958, p. 117. See, however, H. Zeldes, G. T. Trammell, R. Livingston and R. W. Holmberg, J. Chem. Phys., 32, 618 (1960).

(2) E. J. Burrell, J. Chem. Phys., 32, 955 (1960).

(3) W. Gordy and C. G. McCormick, THIS JOURNAL, 78, 3243 (1956); C. F. Luck and W. Gordy, ibid., 78, 3240 (1956).

(4) B. Smaller and M. S. Matheson, J. Chem. Phys., 28, 1169 (1958).

(5) R. H. Luebbe and J. E. Willard, THIS JOURNAL, 81, 761 (1959).

(6) R. G. Bennett, R. L. McCarthy, B. Nolin and J. Zimmerman, J. Chem. Phys., 29, 249 (1958).

(7) H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, THIS JOURNAL, 82, 766 (1960).

(8) R. G. Bennett, P. C. Hoell and R. P. Schwenker, Rev. Sci. Instr., 29, 659 (1958).

Results

Structure of the Radicals.—The first derivative of the e.p.r. spectrum of irradiated N-ethylpropionamide (Fig. 1A) is a 5-line spectrum with absorption peak heights (of the zeroth derivative) in the ratio 1:4:6:4:1. This is the peak height distribution for an unpaired electron in the environment of four equivalent hydrogen atoms (hyperfine splitting). The structure of the ethylpropionamide radical is shown in Fig. 2, where the dashed line encloses those atoms that can interact with the unpaired electron.
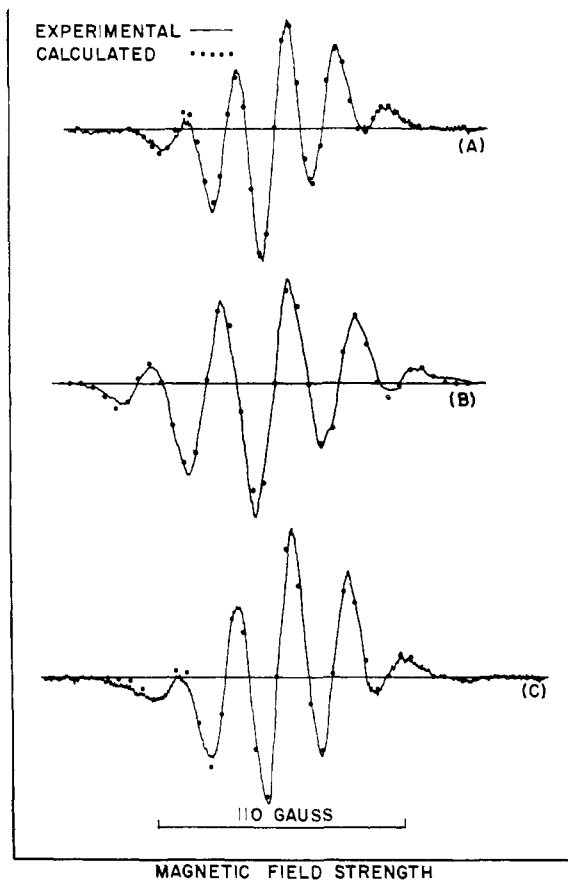
Fig. 1.—First derivative of the e.p.r. spectrum of irradiated (A) N-ethylpropionamide (B) N-ethylbutyramide and (C) N-ethylhexanamide.
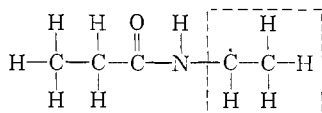
Fig. 2.

Even though these four hydrogen atoms are not chemically equivalent, they are nearly equivalent in their interaction with the unpaired electron. Molecular orbital and valence bond calculations for aliphatic radicals allow this near equivalence.[9,10]

The e.p.r. spectrum of irradiated N-ethylbutyramide (Fig. 1B) is also a "14641" spectrum, again indicating four nearly equivalent hydrogen atoms interacting with the unpaired electron. The ethylbutyramide radical is shown in Fig. 3.

(9) D. B. Chestnut, *J. Chem. Phys.*, **29**, 43 (1958).
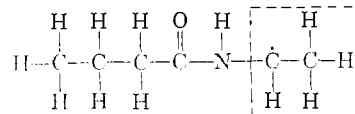(10) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

Fig. 3.

The e.p.r. spectrum of irradiated N-ethylhexanamide (Fig. 1C) is again a "14641" spectrum. The structure of the radical is shown in Fig. 4.
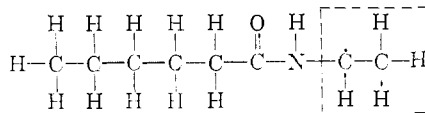
Fig. 4.

Thus, in these three examples where an ethyl-group is substituted on the amide nitrogen, the e.p.r. spectrum is the same for each amide regardless of the structure of the carbonyl side of the molecule.

Conversely, if the N-substituent is changed, the e.p.r. spectrum changes. The e.p.r. spectrum of irradiated N-(n-propyl)-propionamide (Fig. 5A) is a 4-line spectrum, with peak heights in the ratio of 1:3:3:1. This indicates interaction of the unpaired electron with three nearly equivalent hydrogen atoms. The structure of the propylpropionamide radical is shown in Fig. 6.

Again, the e.p.r. spectrum of irradiated N-(n-propyl)-butyramide (Fig. 5B) is a 4-line "1331" spectrum for which the structure is shown in Fig. 7.

Similarly, the e.p.r. spectrum of irradiated N-(n-hexyl)-propionamide (Fig. 5C) is a 4-line "1331" spectrum having the structure shown in Fig. 8. Here, the hexyl group furnishes the same local environment for the radical as does the N-propyl group above.

Thus, several generalizations may be made: (1) Under irradiation a hydrogen atom is removed from a CH group adjacent to the amide nitrogen atom. (2) The interaction of the unpaired electron extends to the H atom on the same carbon and to the hydrogen atoms on the carbon atom next to the free radical site but no further. (3) The hydrogen on the nitrogen atom does not overlap appreciably with the wave function of the unpaired electron (*i.e.*, does not interact to give hyperfine splitting).

The free radical site alpha to the amide nitrogen found by e.p.r. is in agreement with the site in irradiated 66-Nylon, a polyamide.[11]

If both α positions are blocked by methyl groups, as they are in N-(t-amyl)-propionamide, then the hydrogen atom β to the nitrogen will be removed by radiation, as shown in Fig. 9. This assignment is made on the basis of the 5-line "14641" e.p.r. spectrum arising from irradiated N-(t-amyl)-propionamide (Fig. 10A).

The same e.p.r. spectrum is observed for irradiated N-(t-amyl)-butyramide (Fig. 10B) and the analogous radical structure assigned; *cf.* Fig. 11.

Irradiated N-(n-propyl-2d_2)-propionamide (deuterated in the N-substituent) shows a broad 2-line e.p.r. spectrum (Fig. 12), indicating interaction of the unpaired electron with one hydrogen atom. The more closely spaced splitting of each

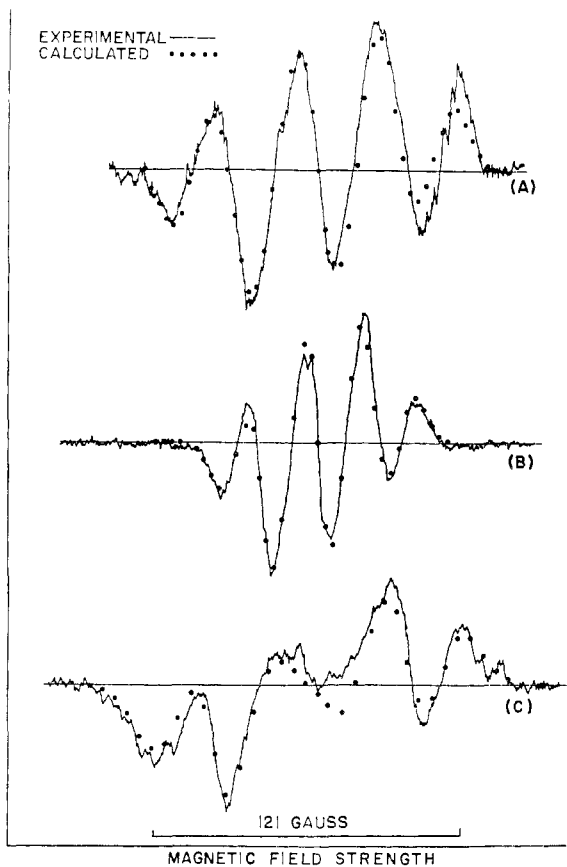(11) J. Zimmerman, *J. Appl. Polym. Sci.*, **2**, 181 (1959).

Fig. 5.—First derivative of the e.p.r. spectrum of irradiated (A) N-(n-propyl)-propionamide, (B) N-(n-propyl)-butyramide and (C) N-(n-hexyl)-propionamide.
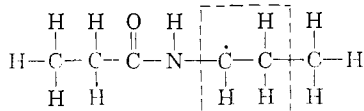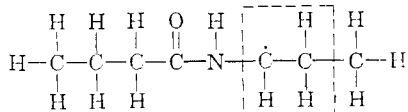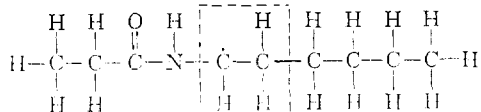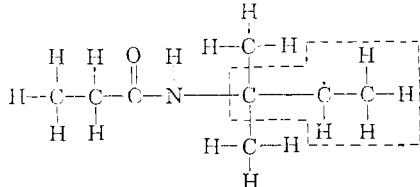

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

broad line due to the deuterium atoms is not re-solved in the experimental spectrum. This is quite consistent with the smaller nuclear moment of deuterium and is accurately predicted in the
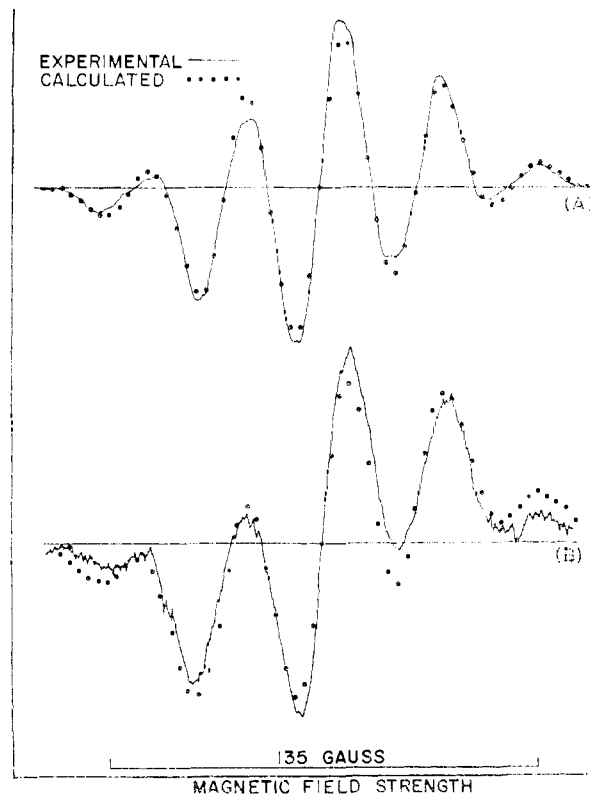

Fig. 10.—First derivative of the e.p.r. spectrum of irradiated (A) N-(t-amyl)-propionamide and (B) N-(t-amyl)-butyramide.
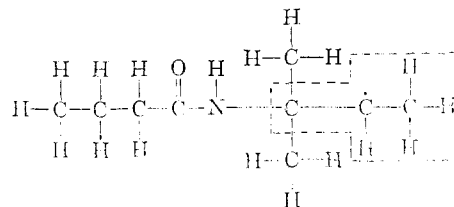

Fig. 11.

computed e.p.r. spectrum. The radical structure is shown in Fig. 13.

For each of the irradiated amides thus far discussed only one kind of radical (one hyperfine pattern) was observed. When N-(neopentyl)-propionamide is irradiated it shows a composite
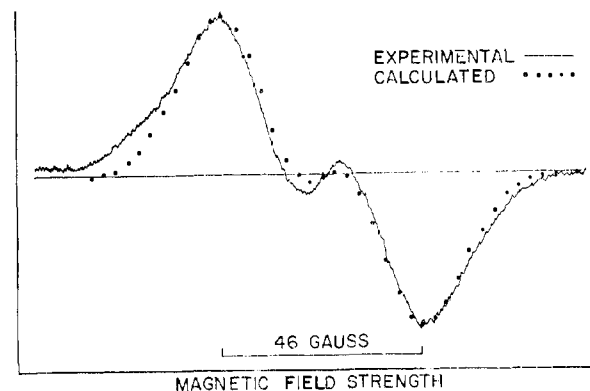

Fig. 12.—First derivative of the e.p.r. spectrum of irradiated N-(n-propyl-2d₂)-propionamide.
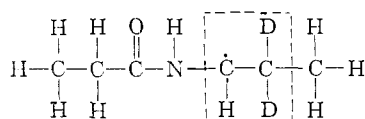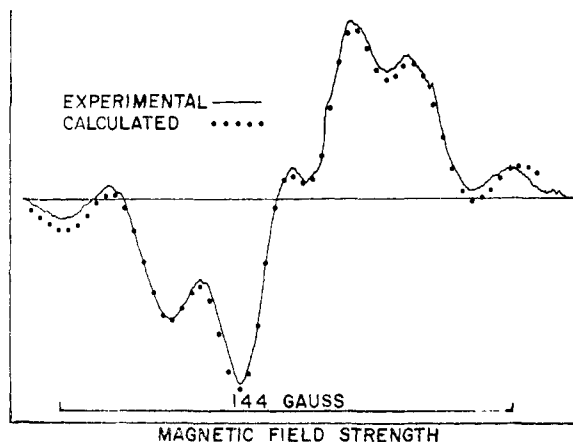
Fig. 13.

Fig. 14.—First derivative of the e.p.r. spectrum of irradiated N-(neopentyl)-propionamide.

e.p.r. spectrum (Fig. 14) representing two radicals in about equal concentrations. The doublet (1:1) component is due to the structure
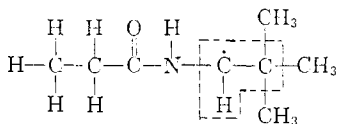

Fig. 15.

The other component is a 5-line "14641" spectrum, indicating four equivalent hydrogen atoms interacting with the unpaired electron. This component probably is due to the structure
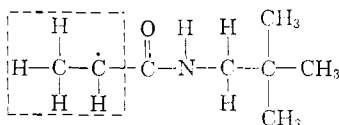

Fig. 16.

This is the only instance where we have assigned the radical site to the carbonyl side of the molecule, although in unsubstituted amides the radical site is known to be on the carbonyl side.[6]

The G-value (number of radicals formed per 100 ev. energy absorbed) for formation of the propyl-propionamide radical was determined by comparison with DPPH and using a flow calorimeter developed in this Laboratory. Its value is 4.7 ± 1.4.

Mechanism of Radical Formation.—It appears that the observed radicals were formed either by direct rupture of the carbon–hydrogen bond or by hydrogen abstraction at the final radical site. The results for irradiated N-(n-propyl-2d_2)-propionamide at −80° preclude the conversion of other radical sites in the amide into the radical site observed by hydrogen atom migration in single jumps along the carbon–carbon chain of the N-

substituent. Consider the hypothetical mechanism for radical formation
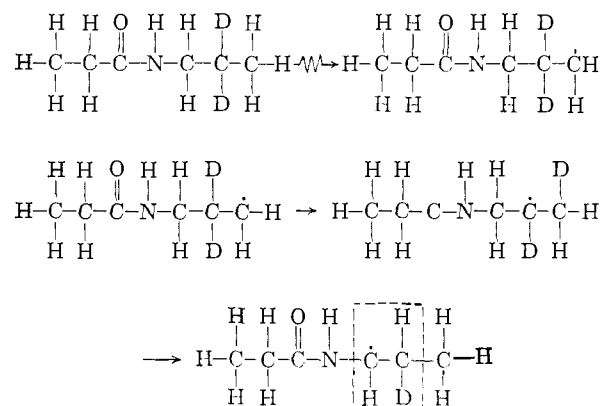
The dashed line encloses those atoms whose nuclei could interact with the unpaired electron. In the hypothetical radical formed through hydrogen atom migration the unpaired electron would interact with one deuterium and two hydrogen atoms instead of one hydrogen and two deuterium atoms as observed (Fig. 13). Since deuterium has a nuclear spin (1) different from hydrogen ($^1/_2$) the e.p.r. spectrum of the hypothetical radical would contain three peaks (with unresolved deuterium splitting) instead of a doublet (with unresolved deuterium splitting) which was observed. Thus, deuteration of the carbon atom next to the preferred radical site allows a decision on the possibility of hydrogen atom migration in single jumps.

Discussion and Conclusions

While single crystal e.p.r. studies are necessary in order to elucidate the detailed electronic structure of a particular radical, it appears equally clear that identification of radicals can be made by means of the e.p.r. spectrum of the (irradiated) poly-crystalline matrix, at least in those cases where spin–orbit coupling is small and where strong dipolar interaction with extremely near neighbors does not occur. These spectra are evidently consistent with (a) small spin–orbit coupling, (b) averaging of moderate dipolar interactions to give broadening of the hyperfine peaks and (c) appreciable overlap of the molecular orbital of the unpaired electron with all the hydrogen nuclei enclosed by the dashed line in the structural formulas.

Only one kind of radical is formed in nine of the irradiated amides and two radicals in the other amide. The G-value for propylpropionamide radicals is in the same range as total G(radical) yields for other compounds. Hence, the specific radical site found in the irradiated amide arises from a selective primary formation of the single kind of radical. The single kind of radical is not merely a small remnant after other radicals have decayed away.