

Photoinitiated Cross-Linking of Low-Density Polyethylene. 7. Initial Radical Reactions with Model Compounds Studied by Spin-Trapping ESR Spectroscopy

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ABSTRACT: The initial radical reactions in the photoinitiated cross-linking of *n*-paraffins (lignocerane and dodecane) and tertiary (isooctane and 3-ethylhexane) and unsaturated (1-hexene, *cis*- and *trans*-3-hexene) hydrocarbons as low-density polyethylene (LDPE) model compounds in the presence of benzophenone (BP) as photoinitiator have been studied by the ESR spectroscopic method using 2,4,6-*tert*-butylnitrosobenzene (BNB) as a spin trap. On the basis of a detailed ESR analysis of the spin adducts formed, several kinds of initial radicals have been detected and identified. These photoinitiated radicals, which combine to form cross-links, are of tertiary, secondary, and primary carbon types formed by hydrogen abstraction from the model compounds by the excited triplet state of BP. The yields are dependent on the probability of hydrogen abstraction from the corresponding group. The evidence shows that tertiary carbon radicals and allyl radicals are the dominating species. Therefore, photo-cross-linking in LDPE model compounds predominantly takes place at sites of tertiary carbon, secondary carbon, and especially allylic carbon when available.

Introduction

Radical intermediates formed in low-density polyethylene (LDPE) during photoinitiated cross-linking initiated by benzophenone (BP) have been studied by the spin-trapping ESR technique.¹⁻³ The results show that photoinitiated cross-linking reactions in LDPE mainly occur by abstraction of tertiary and secondary bonded hydrogens and combination of the polymer radicals formed. H-shaped cross-links appear to dominate. The results are difficult to interpret due to the limited resolution of the ESR spectra of the macroradicals, an effect of the intrinsic characteristics of the polymer chains, e.g. variations in configuration and conformation related to molecular weight and molecular weight distribution, branched structure, unsaturated bonds, etc.

In order to resolve these uncertainties in the study of the polymers,³ the mechanism of photoinitiated cross-linking has been reexamined using model compounds of low molecular weight. The advantages are that the ESR spectra of spin-trapped radicals of low molecular weight have narrow lines and are easy to interpret and that the various models can be studied one at a time. According to our previous work,⁴ commercial LDPE polymers usually contain small amounts of unsaturated bonds (either as end groups or inner groups) in addition to branch points and paraffin chain segments. Therefore, the following three kinds of model compounds for LDPE have been selected: *n*-paraffins, branched hydrocarbons, and unsaturated hydrocarbons containing allylic hydrogen.

The purpose of this study of model compounds for LDPE is to elucidate the nature of the reactions leading to cross-links and further improve the efficiency of the photo-cross-linking of PE by selecting suitable cross-linking systems. This paper presents the results obtained from spin-trapping with 2,4,6-*tert*-butylnitrosobenzene (BNB) of radicals formed during photoinitiated cross-linking of the model compounds with benzophenone (BP) as initiator.

Experimental Section

Materials. Seven model compounds for LDPE were used in this work: two *n*-paraffins, lignocerane (C₂₄H₅₀, mp 51 °C) from Tokyo Kasei Kogyo Co. and dodecane (C₁₂H₂₆, purity ≥98%, *d* = 0.748, bp 209–212 °C) from Fluka; two paraffins with branched structure, isooctane (C₈H₁₈, purity ≥98%, *d* = 0.688–0.693) from Hangzhou Refinery and 3-ethylhexane from Tokyo Kasei Kogyo Co.; three unsaturated compounds, 1-hexene (purity ≥98%) from Fluka and *cis*- and *trans*-3-hexene from Tokyo Kasei Kogyo Co.

Benzophenone (BP, mp 47–49 °C, chemical purity) from Shanghai Reagent Plant No. 1 is used as a photoinitiator. The spin-trapping compound 2,4,6-*tert*-butylnitrosobenzene (BNB, purity ≥98%, mp 172–173 °C) was obtained from Aldrich.

All the above chemicals are commercial products used as received.

Sample Preparation. Photoinitiator (BP, 0.01 M) and spin-trapping compound (BNB, 0.01 M) were dissolved in a liquid model compound (MD) at room temperature to produce the samples for irradiation. The sample was poured into a quartz ESR tube of special design,⁵ which was evacuated with the freeze-thaw method to a vacuum of 5 × 10⁻⁵ Torr and filled with highly pure nitrogen repeatedly for 0.5 h, then irradiated with UV light (high-pressure mercury lamp, GGU-500 W, made in Shanghai) for 3–5 min at room temperature and immediately analyzed in the ESR spectrometer. The sample for model compound *n*-C₂₄H₅₀, a solid at room temperature, was prepared by adding BP (0.01 M) and BNB (0.01 M) to *n*-C₂₄H₅₀ powder and then melting by immersion in warm water (55 °C) to obtain homogeneous mixing. The *n*-C₂₄H₅₀/BP/BNB sample was evacuated and warmed to different temperatures for the ESR measurements, as indicated in the tables and figures. Other conditions and procedures are the same as those for the liquid samples.

ESR Measurements. Control irradiation experiments were first carried out with the pure model compound (MD), the spin trap (BNB), and the solutions MD/BP, MD/BNB, and BP/BNB under the same conditions as the MD/BP/BNB sample. No detectable amounts of radicals were found in the control experiments.

The ESR spectra of spin-adduct radicals were observed for the irradiated samples with an X-band ESR spectrometer, Bruker ER 200 D, with a variable-temperature controller, operated at 9.4 GHz with 100-kHz modulation. The *g* value and the hy-

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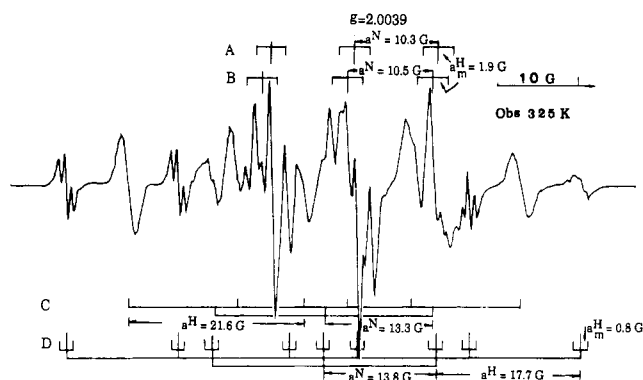


Figure 1. ESR spectrum recorded at 325 K from the n -C₂₄H₅₀/BP/BNB system, UV-irradiated and measured at 1×10^{-4} Torr and room temperature.

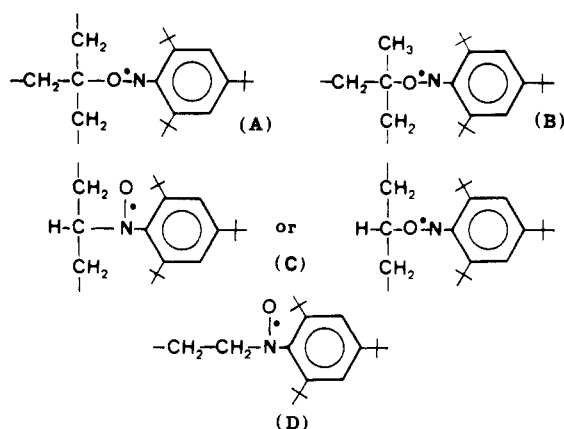


Figure 2. Spin-adducts assigned as present in the n -C₂₄H₅₀/BP/BNB system irradiated with UV light.

perfine splitting constants were measured by the same methods reported in a previous paper.³

Results and Discussion

n -Paraffins. The two n -paraffins C₂₄H₅₀ and C₁₂H₂₆ were used as models for long chain segments of LDPE. The ESR spectrum for n -C₂₄H₅₀/BP/BNB obtained at 325 K after UV irradiation for 4 min at room temperature and in vacuum (10^{-4} Torr) is shown in Figure 1. The spectrum contains four components A–D represented by the stick diagrams in Figure 1. These components are assigned to the anilino or nitroxide spin-adducts A–D, respectively, as shown in Figure 2.

The spin-adducts A and B represent two types of tertiary carbon radicals which form H-type and Y-type cross-links in Silverman's nomenclature.⁶ Originally, there is no tertiary bonded hydrogen in the model molecule (the n -paraffin). Therefore, the tertiary carbon radical formed

by hydrogen abstraction originates from cross-linked dimers of two C₂₄H₅₀ molecules. The spin-adduct C is assigned to a secondary carbon radical generated by hydrogen abstraction from the CH₂ segments of the model molecule. The spin-adduct has either an anilino- or a nitroxide-type structure. The spin-adduct D is assigned to the small amount of chain end methylene radicals formed by hydrogen abstraction from methyl end groups. The ESR parameters and the assignments of the spectra to the radicals (Table I) are in good agreement with those reported by Tabata et al. for cross-linking of n -eicosane by γ -irradiation.^{7–9} The difference is that the chain end radical ($\text{--H}_2\text{C}^\bullet$) is also detected in our experiments with parameters fitting those reported in the literature.¹⁰

The spin-adducts B and D (Figure 2) were not detected in the ESR spectra for LDPE spin-adducts with tetramethylnitrosobenzene (ND) and tri-*tert*-butylnitrosobenzene (BNB).^{1–3} This is reasonable because the LDPE macromolecules contain few end groups (--CH_3) compared with the model compounds.

The sample n -C₂₄H₅₀/BP/BNB was UV-irradiated at room temperature and then heated to 403 K. Its ESR spectra were recorded at 403, 373, and 325 K in this order to study the stability of the compounds (Figure 3). It is evident that the main signal (component A) assigned to the tertiary spin-adduct radical A is stable (compared with Figure 1) while component C assigned to spin-adduct C has decreased and components B and D assigned to spin-adducts B and D, respectively, have disappeared. The latter two radicals, located at the chain ends, are more mobile and therefore less stable and decay faster at higher temperatures. All spin-adducts of BNB and other nitroxide spin traps decompose at elevated temperatures due to thermal motion. When a chain end radical combines with an A or C radical, a long chain branch of Y-structure forms, while two A or C radicals in the central parts of the C₂₄H₅₀ combine to give an H-cross-link according to Silverman's nomenclature.⁶ These data indicate that H-cross-links are expected to dominate in LDPE photo-cross-linked at melt temperature.

The ESR spectrum of the spin-adduct from n -C₁₂H₂₆/BP/BNB (Figure 4) at room temperature, recorded after UV irradiation under nitrogen for 5 min is almost the same as that of n -C₂₄H₅₀/BP/BNB and is assigned to radicals of the same structure (Figure 1). The detailed ESR data of the spin-adducts A–D for n -C₁₂H₂₆ and the assigned radicals A–D are listed in Table I.

The ESR data for the model compounds are interpreted as two main photoinitiated reactions: (i) The excited ³(BP)* first abstracts hydrogen from methylene groups to form --CH-- radicals. (ii) After combination of these radicals, the excited ³(BP)* further abstracts labile tertiary hydrogen to form tertiary carbon radicals.

Table I
ESR Parameters of Spin-Adduct Radicals [R–BNB]• from n -Paraffins

paraffin	R•	[R–BNB]• spin-adducts			
		<i>g</i>	<i>a</i> ^N , G	<i>a</i> ^{H_β} , G	<i>a</i> ^{H_m} , G
(A) n -C ₂₄ H ₅₀ (at 1×10^{-4} Torr)	$\text{--CH}_2\text{--}\dot{\text{C}}\text{--CH}_2\text{--}$ (A)	2.0039	(A) 10.3		1.9
	$\text{CH}_2\text{--}$		(B) 10.4		1.9
(B) n -C ₁₂ H ₂₆ (N ₂)	$\text{--CH}_2\text{--}\dot{\text{C}}\text{--CH}_3$ (B)	2.0045	(A) 10.5		1.9
	$\text{CH}_2\text{--}$		(B) 10.5		1.9
	$\text{--CH}_2\text{--}\dot{\text{C}}\text{H--CH}_2\text{--}$ (C)	2.0061	(A) 13.3	21.6	^a
			(B) 13.3	21.7	^a
	$\text{--CH}_2\text{--}\dot{\text{C}}\text{H}_2$ (D)	2.0062	(A) 13.8	17.9	0.8
			(B) 13.9	17.8	0.8

^a Not resolved.



Figure 3. ESR spectra of the $n\text{-C}_{24}\text{H}_{50}$ /BP/BNB sample irradiated at room temperature and recorded at different temperatures in the following order: (A) 403 K; (B) 373 K; (C) 325 K.

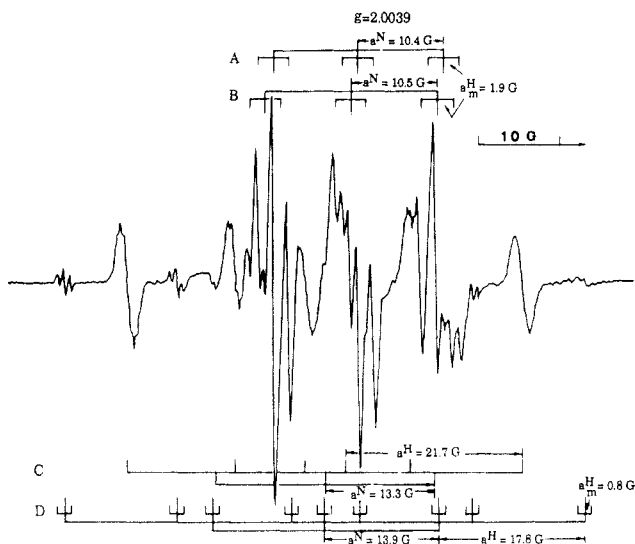


Figure 4. ESR spectrum recorded at room temperature for the $n\text{-C}_{12}\text{H}_{26}$ /BP/BNB system UV-irradiated under a nitrogen atmosphere.

Branched Hydrocarbons. Isooctane and 3-ethylhexane are model compounds for the branching units of LDPE chains, each containing only one tertiary bonded hydrogen but of different structure. The samples isooctane/BP/BNB (1) and 3-ethylhexane/BP/BNB (2) were UV-irradiated at room temperature, sample 1 for 3 min under N_2 atmosphere and sample 2 for 5 min in vacuum. The ESR spectra are shown in Figures 5 and 6.

Two spectral components are identified in Figure 5 and assigned to the radicals given in Table II. The main component is a triplet of triplets due to the nitrogen (10.2

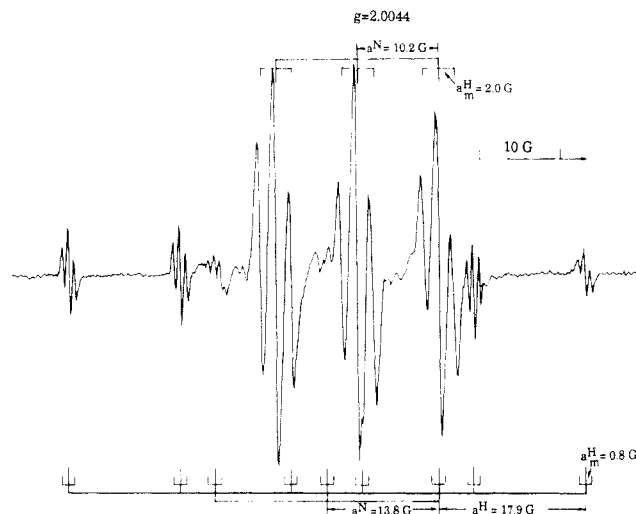


Figure 5. ESR spectrum of the 2,2,4-trimethylpentane/BP/BNB (isooctane) system, irradiated with UV light under a nitrogen atmosphere.

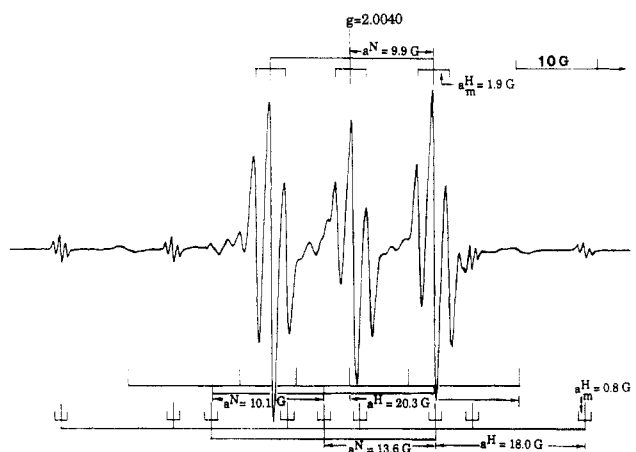


Figure 6. Spin-adduct radicals recorded for the 3-ethylhexane/BP/BNB sample UV-irradiated at 5×10^{-5} Torr.

G) and the two meta hydrogens (2.0 G) of the phenyl group in the anilino-type spin-adduct, as previously described in our work.³ The observed ESR coupling parameters agree with those published.^{10,11} The weaker spectral component is assigned to a primary radical $\cdot\text{CH}_2$ formed by hydrogen abstraction from one of the five methyl groups of isooctane (Table II). The spectral component is a triplet of triplets of small triplets assigned to nitrogen (13.8 G), the two methylene hydrogens (17.9 G), and the two meta hydrogens (0.80 G) of the phenyl groups in BNB with the spin trap in nitroxide form. Hydrogen abstraction from methyl groups would occur in measurable amounts due to the high concentration of methyl groups in isooctane. There is no evidence of hydrogen abstraction from methyl groups in LDPE.³ There is no indication of hydrogen abstraction from the CH_2 group in isooctane (Figure 5), probably due to steric hindrance of the five methyl groups.

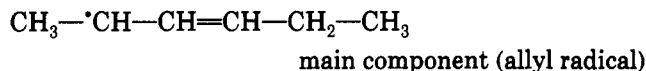
The ESR spectrum of spin-adducts from UV-irradiated samples of 3-ethylhexane/BP/BNB contains three components (Figure 6). The main component is identical with that of isooctane (Figure 5) and assigned to the tertiary radical (Table II). The second component is also the same as that of isooctane, with nearly the same hyperfine coupling constants. The third component is very weak, a triplet ($a^{\text{N}} = 10.1$ G) of doublets ($a^{\text{H}}_{\beta} = 20.3$ G), assigned to a radical formed by hydrogen abstraction from a CH_2 group of which there are four in the 3-ethylhexane molecule having less steric hindrance than isooctane.

The results for hydrogen abstraction from isooctane and 3-ethylhexane show that tertiary bonded hydrogen ($>\text{CH}-$) is easier to abstract in photo-cross-linking with BP than are secondary ($-\text{CH}_2-$) and primary bonded hydrogens ($-\text{CH}_3$). This is well in line with the known bond dissociation energies (Table III) for the three types of hydrogens.^{12,13} It has also been reported¹⁴ that the relative rate constant ratio for hydrogen abstraction from primary, secondary, and tertiary hydrocarbons of low molecular weight is 1:40:300. For a model compound with steric hindrance, the abstraction of hydrogen at primary and secondary carbons to form the corresponding radicals may still be favored by high concentrations of CH_2 and CH_3 . Tertiary hydrogens and end groups (CH_3) in LDPE are few in number compared with the secondary hydrogens in CH_2 groups.

Unsaturated Hydrocarbons. Three kinds of unsaturated compounds, 1-hexene with a double bond at the end group and two with an inner double bond, *cis*- and *trans*-3-hexene, were used as model compounds. It is reported that the small amounts of double bonds in commercial LDPE samples are important during the cross-linking of the polymer by γ -irradiation.¹⁵⁻¹⁸

The ESR spectrum of a 1-hexene/BP/BNB sample, UV-irradiated for 3 min under nitrogen atmosphere, is shown in Figure 7. Only one spectral component is detected, a triplet of doublets with coupling constants 21.6 and 13.4 G with the g value 2.0061. It is assigned to spin-trapped allyl radicals. The broad lines of this spectrum (Figure 7) may be due to overlap of spin-trapped allyl and secondary carbon radicals, which have similar g values and hyperfine coupling constants. These two ESR spectra would be difficult to resolve and differentiate.

Figures 8 and 9 show the ESR spectra recorded for *cis*- and *trans*-3-hexene samples after UV irradiation in vacuum (1×10^{-5} Torr) but otherwise under the same conditions as used for 1-hexene. In Figure 8, the dominant spectral component is assigned to a spin-trapped allyl radical, a triplet ($a^{\text{N}} = 10.1$ G) of doublets ($a^{\text{H}_\beta} = 20.3$ G) of small triplets ($a^{\text{H}_\text{m}} = 0.8$ G), due to coupling with the two meta hydrogens of the phenyl group in the spin trap. There are also small amounts of two other components. One is a triplet ($a^{\text{N}} = 10.9$ G) of triplets ($a^{\text{H}_\text{m}} = 1.9$ G) which was tentatively assigned to a spin-trapped tertiary carbon radical. The other component is a triplet ($a^{\text{N}} = 13.3$ G) of triplets ($a^{\text{H}_\beta} = 17.6$ G) of small triplets ($a^{\text{H}_\text{m}} = 0.8$ G) assigned to a spin-trapped $-\text{CH}_2$ radical formed by hydrogen abstraction from a CH_3 group. These three radicals should be



The *trans*-3-hexene gives an ESR spectrum (Figure 9) which is analogous to that of *cis*-3-hexene (Figure 8). The hyperfine coupling constants of the main component are slightly different, and the amounts of the minor components greater. The assignment of the three spectral components is the same as for *cis*-3-hexene.

The ESR parameters agree with previous measurements^{19,20} and the assigned radicals from 1-hexene and *cis*- and *trans*-3-hexene are given in Table IV. There is good evidence for assignment of the main radical com-

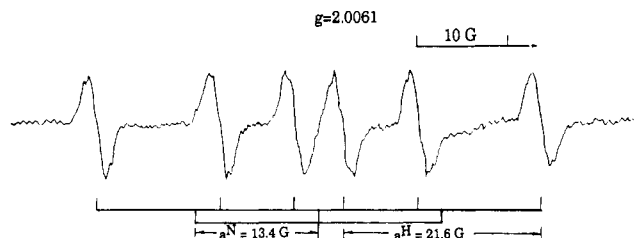


Figure 7. ESR spectrum recorded at room temperature for 1-hexene/BP/BNB UV-irradiated under a nitrogen atmosphere.

Table II
ESR Parameters of Spin-Adduct Radicals $[\text{R-BNB}]^{\bullet}$ from Tertiary Hydrocarbons

R $^{\bullet}$	[R-BNB] $^{\bullet}$ spin-adducts			
	g	a^{N} , G	a^{H_β} , G	a^{H_m} , G
Isooctane (N_2)				
	2.0044	10.2		2.0
	2.0063	13.8	17.9	0.8
3-Ethylhexane (at 1×10^{-5} Torr)				
	2.0040	9.9		1.9
	2.0061	10.1	20.3	^a
	2.0062	13.6	18.0	0.8

^a Not resolved.

Table III
C-H Bond Dissociation Energies^{12,13}

compd	C-H (kcal/mol)	compd	C-H (kcal/mol)
$\text{CH}_3-\text{CH}_2-\text{H}$	98	$\text{H}_2\text{C}=\text{CHCH}_2-\text{H}$	88
$(\text{CH}_3)_2\text{CH}-\text{H}$	95	$\text{H}_2\text{C}=\text{CH}-\text{H}$	104
$(\text{CH}_3)_3\text{C}-\text{H}$	91		

ponents to allyl radicals. The assignments of the minor spectral components for *cis*- and *trans*-3-hexene are made with the evidence available but they are only tentative. Further studies of other model compounds may give additional evidence for the assignment of the minor spectral compounds.

Conclusions

(1) In photoinitiated cross-linking reactions of aliphatic hydrocarbons as model compounds for low-density polyethylene (LDPE) using benzophenone (BP) as initiator, allylic and tertiary bonded hydrogens are more easily abstracted than primary and secondary bonded hydrogens.

(2) The resulting radicals have been spin-trapped, and their structure has been analyzed by ESR spectroscopy. On the basis of these data, the photo-cross-linking mechanism for LDPE has been interpreted as combination reactions of the radicals formed by abstraction of the various hydrogens mentioned in point 1.

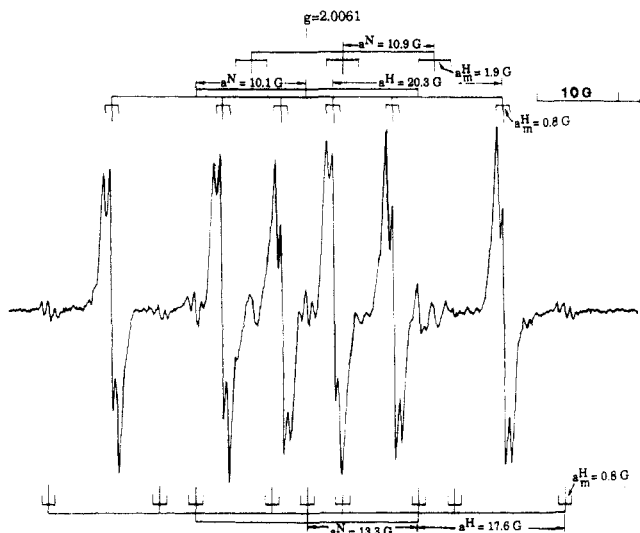


Figure 8. Spin-adduct radicals observed for *cis*-3-hexene/BP/BNB UV-irradiated at 5×10^{-5} Torr.

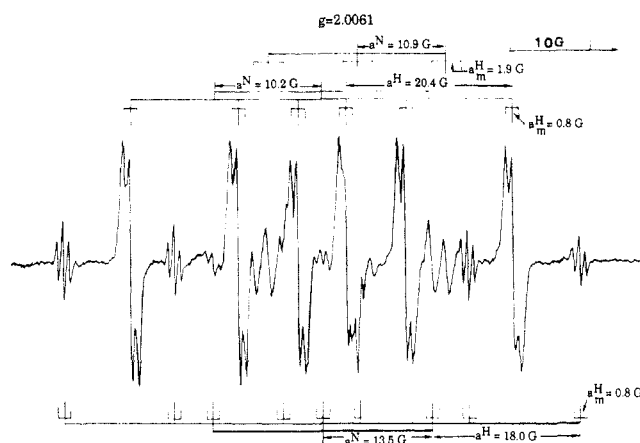


Figure 9. Spin-adduct radicals observed for *trans*-3-hexene/BP/BNB UV-irradiated at 5×10^{-5} Torr.

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Table IV
ESR Parameters of Spin-Adduct Radicals [R-BNB] \cdot from Unsaturated Compounds

R \cdot	[R-BNB] \cdot spin-adducts			
	<i>g</i>	<i>a</i> ^N , G	<i>a</i> ^{H_β} , G	<i>a</i> ^{H_m} , G
1-Hexene (N ₂)				
CH ₂ =CH- $\dot{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$	2.0061	13.4	21.6	
<i>cis</i> -3-Hexene (at 1×10^{-5} Torr)				
	2.0061	10.1	20.3	0.8
	2.0062	13.3	17.6	0.8
	2.0036	10.9		1.9
<i>trans</i> -3-Hexene (at 1×10^{-5} Torr)				
	2.0061	10.2	20.4	0.8
	2.0062	13.5	18.0	0.8
	2.0036	10.9		1.9

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Registry No. LDPE, 9002-88-4; BP, 119-61-9; lignoceran, 646-31-1; dodecane, 112-40-3; isooctane, 540-84-1; 3-ethylhexane, 619-99-8; 1-hexene, 592-41-6; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8.