The entropy estimate for the benzyl radical has been made as follows.

$S°_{298}(C_6H_5CH_2\cdot) = S°_{298}(C_6H_5CH_3) - 0.8$ (loss of hydrogen deformation mode) $+ R \ln 3$ (symmetry changes) $+ R \ln 2$ (electronic degeneracy) $- 3.0$ (loss of internal rotation in resonance stiffened radical) $= S°_{298}(C_6H_5CH_3) - 0.3$

It was assumed that this difference did not alter with temperature. This was considered uncertain to ±1 gibbs/mole. In conjunction with the listed entropies,[2] this gave $\Delta S°_{1,2}(500°K) = +4.51 \pm 1$ and $\Delta S°_{3,4}(500°K) = -6.93 \pm 1$ gibb/mole. Thus the ratios A_1/A_2 and A_3/A_4 could then be evaluated and the individual A factors separated by substitution of A_4 and A_2/A_3. The Arrhenius parameters for k_4 are a refinement of our measured value obtained by assuming the global rate constant is correct and adjusting the activation energy (within its standard error) to give the correct toluene bond strength.

A comparison of this system with similar systems[12a] involving $I_2 + RH$ reveals that the A factors here are all about $10^{2.5}$ lower than those where R is not a resonance-stabilized radical. This indicates that the transition states are extremely tight for reactions $1 \rightleftarrows 2$ and $3 \rightleftarrows 4$. A similar stiffening was found for the case where $R \equiv$ methylallyl[25a] or allyl.[25b]

The Reaction of Hydrogen Atoms with Some Conjugated Ring Systems at 77°K[1]

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Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received October 22, 1965*

Abstract: Binary mixtures of naphthalene with methanol and ethanol have been irradiated with X-rays at 77°K and studied by esr methods. Previous work has determined that, upon irradiation, the hydroxyl hydrogen is liberated and subsequently adds on to the conjugated ring system. With naphthalene, the hydrogen atom adds on in the α position. Molecular orbital calculations of the cyclohexadienyl radical and the corresponding naphthalene radical show good agreement with the data obtained.

This paper presents further studies on the irradiation of binary mixtures of conjugated ring systems and simple alcohols. Earlier studies[2] utilizing benzene in methanol and ethanol reveal that, upon irradiation at 77°K, a hydroxyl hydrogen atom is released. This hydrogen atom then can form H_2 by combining with another hydrogen atom and by abstraction of a hydrogen from the alcohol matrix or can add on to the benzene ring to form the cyclohexadienyl radical. At temperatures slightly warmer than that of liquid nitrogen, all other radical species decay, and the esr spectrum of the cyclohexadienyl radical is obtained with measured splitting constants that agree with other work.[3,4] In this study, naphthalene and various methyl-substituted benzenes such as toluene, xylene, and mesitylene were studied in mole percentages ranging from 1 to 5 mole %.

Experimental Section

Reagent grade chemicals without further purification were used throughout this study. The isotopically substituted naphthalene-d_8 and methanol-d were obtained from Volk Radiochemical Company and have a minimum isotopic purity of 98 atom %. The irradiation procedure and detection equipment have been discussed elsewhere.[2] The solubility of naphthalene in both methanol and ethanol is much less than 5 mole %. The procedure used was to make a concentrated solution of naphthalene in the alcohol, and then dilute with more alcohol until the solution formed glassy spheres when droplets were dropped into liquid nitrogen. The dilution was a factor of 2 to 4 times that of concentrated solution. A small amount of ethyl ether had to be added to the mesitylene-methanol solution so that a glass could be formed. The same amount of ether was added to the xylenes also without altering the results.

Results and Discussion

A. Naphthalene. Figure 1 shows the spectrum obtained of the naphthalene radical in methanol after warming up and permitting the methanol triplet to decay. The spectrum consists of a 37-gauss 1:2:1 triplet due to two hydrogen atoms at position 1, the site attached by the free hydrogen atom. These lines are then split into 12.8-gauss 1:2:1 triplets due to the nearly equivalent hydrogens at positions 2 and 4. Position 3 should give a doublet splitting of 3.1 gauss, but it is not resolvable. Positions 5 through 8 have very low spin density as will be shown by the calculations.

Figure 2 shows the results of the isotopic runs. In Figure 2A, naphthalene was irradiated in a matrix of MeOD. The deuterium from the matrix adds to position 1, and the hydrogen doublet from position 1 is clearly visible. The splittings due to the hydrogens at sites 2 and 4 are visible, but one has some trouble (as was the case with C_6H_6 in MeOD) finding the deuterium triplet. Figure 2B shows $C_{10}D_8$ in MeOD and the 1:2:3:2:1 quintuplet from the two sp^3 deuteriums is readily visible. Figure 2C shows $C_{10}H_8$

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[1] This investigation was supported in part by Research Grant GM 5144 from the Division of General Medical Sciences, Public Health Service, National Institutes of Health.

[2] J. A. Leone and W. S. Koski, *J. Am. Chem. Soc.*, **88**, 224 (1966).

[3] S. Ohnishi, T. Tanei, and I. Nitta, *J. Chem. Phys.*, **37**, 2402 (1962).

[4] H. Fischer, *Kolloid-Z.*, **180**, 64 (1964).

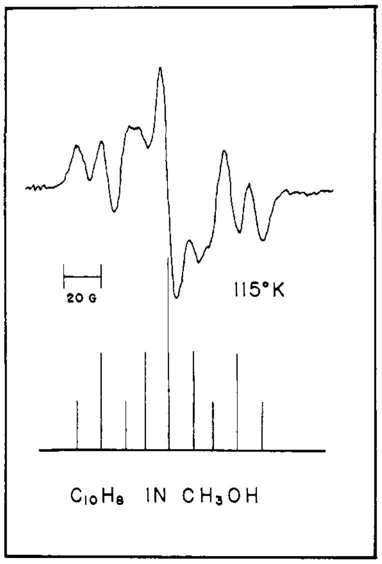

Figure 1. The esr spectrum of an irradiated naphthalene in methanol solution at 115°K.

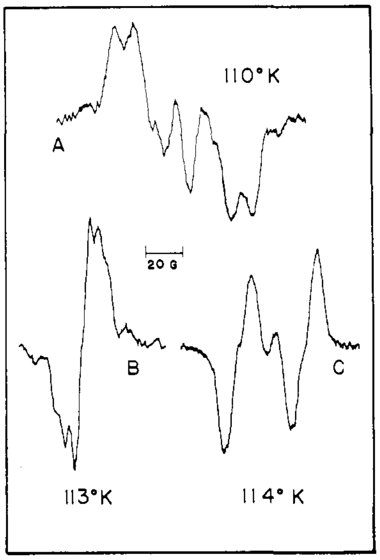

Figure 2. The esr spectra of irradiated isotopic mixtures of naphthalene in methanol solutions: (A) naphthalene in methanol-*d*; (B) naph thalne-d_8 in methanol-*d*; (C) naphthalene-d_8 in methanol.

in MeOH. Here the sp^3 hydrogen doublet can easily be seen while the deuterium triplets are poorly resolved. The resolution anomalies are probably due to a combination of changing matrix properties and an anisotropic effect of radicals in a rigid media. As in the benzene case, the use of CD_3OH gave results the same as with MeOH.

Naphthalene and its deuterated analog were run in ethanol with the same results. Figure 3A shows naphthalene in ethanol while 3B shows naphthalene-d_8 in ethanol. The spectra are the same as those obtained for the methanol system except for a slight distortion in the center due to a residual ethanol peak.

Larger fused ring systems were tried, but because of a solubility problem the radical formed was in too low a concentration to be detected.

B. Methyl-Substituted Benzenes. Methyl-substituted benzenes in methanol also exhibited strong tendencies to scavenge the hydrogen atom released by the methanol. With the addition of the methyl side groups, however, there appears to be two competing reactions. The hydrogen atom can add to the benzene ring to give the cyclohexadienyl-type radical, or it can abstract a hydrogen from a methyl group leaving a benzyl-type structure.

Toluene, *o*-, *m*-, and *p*-xylene, and mesitylene all give a large 50-gauss triplet in methanol and a 50-gauss doublet in methanol-*d*. Regardless of the matrix, they all have a triplet of 17- to 18-gauss splitting on the center peak of the large triplet (or between the large doublet if methanol-*d* is used) which is the benzyl-type radical.[5]

The spectra are poorly resolved, and thus an assignment cannot be made as to where the hydrogen atom adds on to the ring, except in the case of mesitylene, where all three positions are equivalent.

MO Calculations

The molecular orbital calculations were carried out using the method of McLachlan.[6] The bonding parameters used were those as given by Streitwieser[7] for the methyl heteroatom model $\equiv$C—X where X is H_2. Here the parameters for the Coulomb integrals are $h_X = 2$ and $h_{C_\alpha} = -0.2$ and for the bonding integral $K_{C-X} = 0.7$. The value for λ was 1.0. Using the familiar formula of McConnell,[8] $a_i = Q\rho_i$, with a value of 28.5 gauss for Q at all sp^2 carbon atoms and a value of 500 gauss for the sp^3 carbon atom position,[9] the calculated splitting constants along with the experimental values are given in Table I for the cyclohexadienyl radical and the corresponding naphthyl radical formed by the addition of a hydrogen atom to position 1 of naphthalene.

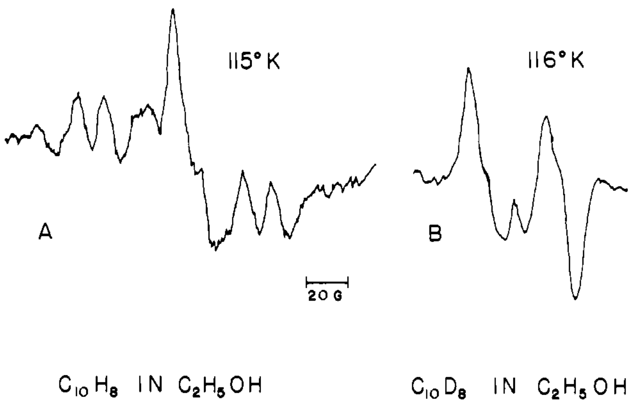

Figure 3. The esr spectra of irradiated isotopic mixtures of naphthalene in ethanol solutions: (A) naphthalene in ethanol; (B) naphthalene-d_8 in ethanol.

The same calculations carried out on the methyl-substituted benzenes using a Coulombic parameter of $h_{C-CH_3} = -0.5$ due to the inductive effect of the methyl groups[7] gave somewhat inconclusive results since the spectra were so poorly resolved and could not be correlated with the results obtained from the calculations.

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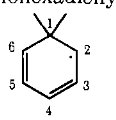
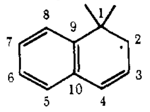
[7] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.

[8] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[9] J. P. Colpa and E. DeBoer, *Mol. Phys.*, **7**, 333 (1964).

Table I

	Method	Hfs and spin densities					
		1	2	3	4	5	6
Cyclohexadienyl 	Expt	47.5	10.4	2.5	10.4	2.5	10.4
		0.095	0.358	−0.088	0.358	−0.088	0.358
	Theory	47.5	10.4	2.6	10.6	2.6	10.4
		0.095	0.358	−0.093	0.373	−0.093	0.358

	Method	Hfs and spin densities							
		1	2	3	4	5	6	7	8
Naphthyl 	Expt	37	12.8	. . .	12.8	. . .	. . .	. . .	. . .
		0.074	0.450		0.450				
	Theory	37	12.9	3.1	11.8	2.5	0.7	2.2	0.5
		0.074	0.454	−0.110	0.415	0.088	−0.02	0.076	−0.014

In the case of toluene and the xylenes, however, the spin density on the sp^3 carbon agreed fairly well with the experimental values.

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Paramagnetic Absorption of Irradiated Glycine[1]

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Contribution from the Biophysics Department, Roswell Park Memorial Institute, Buffalo, New York. *Received September 15, 1965*

Abstract: Single crystals of deuterated glycine, $^+ND_3$-CH_2-$COO,^-$ were irradiated at 77°K and subsequently warmed to 165°K. Well-defined electron spin resonance spectra were observed due to either CH_2COO^- or CH_2-COOD. The intensities of sixteen allowed and "forbidden" transitions calculated on the basis of a simple model agree well with the observed hyperfine patterns.

The use of electron spin resonance (esr) spectroscopy for the study of radiation damage in organic materials began about 11 years ago.[2] Probably the most thoroughly investigated organic material to date has been irradiated glycine which crystallizes as the zwitterion $NH_3^+CH_2COO^-$. The room-temperature absorption pattern of X-irradiated glycine is complicated by the presence of more than one kind of free radical. The absorption has been variously assigned to the free radicals $CH_2NH_3^+$, $CH_3CO_2^-$, NH_2, NH_4, and $NH_3^+CHCO_2^-$.[2-4]

In this investigation low temperature was used to stabilize an earlier phase of the radiation damage process. Single crystals of glycine were irradiated at low temperature, subsequently warmed to a prescribed temperature, and studied by esr spectroscopy. Unlike the room temperature absorption, the observed spectra were definitive for all orientations of the crystals.

Experimental Method

Monoclinic crystals of glycine were grown by slow evaporation of aqueous solution. The crystals belong to the space group $P2_1/n$ with four molecules per unit cell. Identification of crystal axes was made optically and checked by X-ray diffraction. Deuterated crystals in which the polar hydrogens of glycine were exchanged for deuterium were grown from heavy water solutions. A single crystal was mounted on the spectrometer sample holder on a quartz fiber and irradiated on a liquid nitrogen bath. The exposure amounted to 1–3 × 10^6 roentgens from a 250-kev X-ray therapy machine. A crystal was then transferred, allowing as little warm-up as possible, to the refrigerated cavity of an esr spectrometer and allowed to warm at the rate of approximately 2°K/min. At any stage of the warming, the crystal could be recooled without affecting the character of the spectrum, although the amount of absorption increased, of course, inversely as the absolute temperature. Having determined at what temperatures spectral changes occur, an alternate procedure was to carry out the warming in a separate dewar and subsequently observe the spectra at 4.2°K. The spectrometer operated at a microwave frequency of 24.0 Gc using superheterodyne detection.

Results

At least three distinct esr spectra can be distinguished as crystals of glycine are allowed to warm following irradiation at liquid nitrogen temperature. There is the low-temperature spectrum which is probably due to ionic species, an intermediate spectrum which is the subject of this report, and the final spectrum which

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(1) Supported in part by Public Health Service Grant GM10873 and Atomic Energy Commission Contract AT(30-1)3558.

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