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Abstract

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ON THE E.P.R. SPECTRUM OF BENZYL RADICALS

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The literature gives theoretical calculations of the spin-density distribution in the radical $C_6H_5CH_2^\bullet$ (^{1,2}). The first experimental attempts to observe hyperfine-structure spectra of the e.p.r. of this radical in solid hydrocarbon glasses were unsuccessful (^{3,4}). In the present work, to obtain $C_6H_5CH_2^\bullet$ radicals, the method developed by V. B. Kazanskii and G. B. Pariiskii (^{5}) for the photolysis of molecules adsorbed on the surface of silica gel was used. Benzyl chloride was used as the starting substance, since it is known that the photodecomposition of $C_6H_5CH_2Cl$ proceeds at the C—Cl bond ($^{6-8}$).

A sample of silica gel (with a specific surface of about 300 m^2/g) weighing about 20 mg was placed in a quartz ampoule with a stopcock and a ground joint for connection to a vacuum system. The silica gel was degassed by pumping at a temperature of 300° and a pressure of 10^{-4}—$5 \cdot 10^{-4}$ mm Hg for 6—7 hr. Then, at room temperature, benzyl chloride vapor was admitted from a volume of 300 ml into the ampoule at a pressure of 0.1 mm Hg (the saturated-vapor pressure of $C_6H_5CH_2Cl$ at room temperature is about 1 mm Hg). After the sample had been kept in the vapor atmosphere for one hour, the ampoule was detached from the vacuum system, immersed in a quartz Dewar with liquid nitrogen, and irradiated with the light of a PRK-7 mercury lamp for 2—4 hr. To record the e.p.r. spectrum, the ampoule was transferred to a foam-plastic Dewar with liquid nitrogen, placed in the resonator of an EPR-2 spectrometer of the Institute of Chemical Physics, Academy of Sciences of the USSR (^{9}).

(Figure: Fig. 1. E.p.r. spectrum of benzyl radicals)

Fig. 1. E.p.r. spectrum of benzyl radicals

The spectrum obtained is shown in Fig. 1. This spectrum may be attributed to $C_6H_5CH_2^\bullet$ radicals, since under these conditions e.p.r. spectra of halogen atoms are not observed (see, for example, (^{5})). The spectrum apparently consists of a triplet with a splitting between components $\Delta H = 16.5 \pm 1$ oersted, each component of which is additionally split into a quadruplet with approximately equal spacings between components $\Delta H = 5.5 \pm 0.5$ oersted. The triplet ($\Delta H = 16.5$ oersted) is apparently due to interaction of the unpaired electron with the protons of the $-CH_2$ group. However, if the unpaired electron were localized only on the carbon atom of the methylene group, the spectrum would be a triplet with $\Delta H = 22$—

23 Oe. The reduced splitting on the protons of the methylene group indicates

delocalization of the unpaired electron in the π-system of the ring, while the splitting of each component of the triplet into a quadruplet indicates interaction of the unpaired electron with three equivalent protons of the ring. On the basis of consideration of the possible structures of the benzyl radical

$$C_6H_5{-}\dot{C}H_2 \qquad \dot{C}_6H_4{=}CH_2 \qquad \dot{C}_6H_4{=}CH_2 \qquad \dot{C}_6H_4{=}CH$$

one may expect localization of positive spin density at positions 1, 3, 5, 7

[[diagram of benzyl radical with ring positions 1–7 and $\dot{C}H_2$ substituent]]

Consequently, the quartet structure of the spectrum can be explained by the interaction of the unpaired electron with the protons in positions 3, 5, 7.

Table 1

	Nos. of the positions of the carbon atom	References to original papers				
	1	2	3,7	4,6	5	
$\Delta H_{i\,\text{exp}}$	16.5 ± 1.0		5.5 ± 0.5		5.5 ± 0.5	
ρ_i	0.770	−0.102	0.16	−0.063	0.137	
ΔH_i	17.3		3.6	1.42	3.08	(1)
ρ_i	0.530	−0.306	0.393	−0.221	0.437	
ΔH_i	11.9		8.9	5	9.8	(2)

Table 1 gives the experimentally obtained values of the splittings $\Delta H_{i\,\text{exp}}$ in the spectrum of the radical $C_6H_5CH_2$. It also gives the values of the spin density ρ_i at each of the carbon atoms, calculated in papers (^{1,2}), as well as the splitting values $\Delta H_{i\,\text{theor}}$ for the various protons, calculated by us on the basis of these data. In the calculation it was assumed that the splitting on a proton is $\Delta H_i = Q\rho$, where $Q = 22.5$ Oe. (^{10,11}). Comparison of the experimental results with the results of theoretical calculations additionally confirms the correctness of the interpretation of the spectrum obtained. As is seen from the data in Table 1, the most complete agreement is observed between the experimental results and the calculation carried out in paper (^{1}).

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Note: Figure translations are in progress. See original paper for figures.