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Abstract

Full Text

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ON THE E.P.R. SPECTRUM OF IRRADIATED FROZEN BENZENE

In one of the previously published works (^{1}), the e.p.r. spectrum of benzene irradiated at 100° K was presented. The spectrum is a well-resolved triplet, each component of which is split into a quadruplet. The central component of the triplet has a substantially greater integral intensity than follows from the binomial law for the distribution of intensities 1 : 2 : 1. Such a spectrum can be explained by the mutual superposition of a 1 : 2 : 1 triplet and a single line whose position coincides with the central component of the triplet. On this basis, and on the basis of chemical data on the radiolysis of liquid C_6H_6 (^{2,3}), the conclusion was drawn that during the radiolysis of solid C_6H_6 two radicals, C_6H_5 and C_6H_7, are formed.

It was assumed that the spectrum with hyperfine structure (h.f.s.) corresponds to the radical

[[structural formula: six-membered ring radical with a dot at position 1 and hydrogens indicated at positions 2-6]]

where the triplet with a total splitting of about 90 oersteds is due to interaction of the unpaired electron with two β-hydrogens (2 and 6), while the additional splitting of each triplet component into four lines is due to interaction with the hydrogen atoms 3, 4, 5.

The single unresolved line was assigned to the radical $C_6H_7\cdot$ (^{1}). Recently, on the basis of a more detailed theoretical analysis, the suggestion has arisen that such an explanation of the observed spectrum cannot be regarded as unambiguous, and that the h.f.s. of $3 \times 4 = 12$ components in the e.p.r. spectrum may also be due to the radical

[[structural formula: cyclohexadienyl-type radical with a $> CH_2$ group and hydrogens indicated]]

if it is assumed that the unpaired electron is localized mainly in positions 2, 4, 6 and that the two hydrogens of the $> CH_2$ group give a triplet with a total splitting of $\sim$ 90 oersteds, while the hydrogen atoms in positions 2, 4, 6 give approximately equal splitting, about 10 oersteds on each*.

Fig. 1. Spectrum of irradiated benzene: a –146° K; b –220° K

Figure 1: Fig. 1. Spectrum of irradiated benzene: a –146° K; b –220° K

By slow warming of the sample to 220° K and holding it at this temperature for 20–30 min. (see Fig. 1), we were able to improve the resolution of the spectrum considerably. At the same time the relative intensity of the central part of the spectrum decreased strongly; apparently, the radical, ···giving a single line, has recombined to a considerable extent. The most important result is the additional splitting of each line of the quartet into a triplet with a total splitting of ~ 7 oersted. (At the center of the spectrum this splitting appears less distinctly because of partial overlap with the single line.) This result completely rules out the possibility of assigning the spectrum with h.f.s. to the radical C_6H_5, since the spectrum of this radical cannot contain more than 18 components. The assumption that the spectrum with h.f.s. is due to the radical $C_6H_7\cdot$ can be confirmed by the following considerations.

From studies of aromatic ion-radicals (^{4}) it is known that the total splitting of the unpaired *p*-electron on hydrogens lying in the plane of the aromatic ring cannot exceed 22–23 oersted (in the absence of alternation in the sign of the spin density). The total splitting obtained in our experiments on all hydrogens of the ring (determined from the total splitting in one component of the main triplet) is 38 oersted.

Fig. 1. Spectrum of irradiated benzene: *a* –146° K; *b* –220° K

This means that there is alternation of spin density in the ring, and the total splitting on the hydrogens corresponding to negative spin density must be equal to

$$\frac{38-22}{2} = 8 \text{ oersted.}$$

From the scheme of the radical $C_6H_7\cdot$ it is seen that negative spin density can be localized only in positions 3 and 5. It follows from this that, if the explanation of the spectrum proposed by us is correct, the additional splitting on each of these hydrogens should be close to $8/2 = 4$ oersted. Experiment gives 3.5 oersted. The assumption that the spectrum with h.f.s. should be assigned to the radical $C_6H_7\cdot$ agrees with the data obtained in work (^{5}), in which the e.p.r. spectrum

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* The large splitting on the hydrogens of the $> CH_2$ group may be due to several causes: to the fact that splitting on β-hydrogens is usually greater than on α-hydrogens; to the fact that interaction with the hydrogens of the $> CH_2$ group occurs not from one position but from two (2 and 6); and, finally, to possible distortions of the geometrical structure of the radical.

is given of radicals formed by the action of hydrogen atoms on polystyrene. In the discussion at the same symposium, Cochran and Adrian reported that they had also obtained a spectrum with hyperfine structure upon photolysis of HJ in the presence of C_6H_6 in a solid matrix.

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