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Abstract

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E.P.R. Spectra and the Kinetics of Radical Accumulation in the Radiolysis of Certain Aromatic Compounds

The aim of the present work was to determine the nature of the radicals formed during the radiolysis of aromatic hydrocarbons, and also to investigate the influence of molecular structure on the yield of radicals. For this purpose, electron paramagnetic resonance (e.p.r.) spectra were recorded for radicals formed under the action of fast electrons (1.6 MeV), and the kinetics of their accumulation was measured. The substances studied are given in Table 1. The method for recording radicals during electron irradiation is described in papers ([1,2]). Irradiation was carried out at current densities from 1.5 to 4.0 μa/cm^2 at temperatures of -124° and $+33^\circ$. The benzene grade was chemically pure. All the other substances studied were obtained from the laboratory of K. P. Lavrovskii at the Institute of Petrochemical Synthesis. These substances were purified by molecular sublimation in a high vacuum.

Table 1

Sample	Temp. -124°	Temp. 33°
Benzene	0.16	
Diphenyl	0.045	
n-Ditolyl	0.08	
o-Ditolyl	0.11	
m-Terphenyl	0.034	0.014
n-Terphenyl	0.046	0.015

Figure 1 shows the e.p.r. spectra of benzene, diphenyl, *n*-terphenyl, and *n*-ditolyl obtained at -124°. The spectra of *m*-terphenyl and *o*-ditolyl are identical to the spectra of their *n*-isomers. At a temperature of $+33^\circ$, the e.p.r. spectra of *n*- and *m*-terphenyl have the same form as at -124°. The e.p.r. spectrum of benzene is a well-resolved triplet, the central component of which has a considerably greater intensity than follows from the binomial law for an intensity

Figure 1

Figure 1: Figure 1

distribution of $1:2:1$. 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. The triplet in the spectrum of benzene can apparently be assigned only to the radical C_6H_5, formed as a result of abstraction of an H atom:

$$C_6H_6 \rightarrow C_6H_5 + H. \tag{1}$$

Interaction of the unpaired electron with two neighboring H atoms gives the three observed lines. It should be noted that the splitting between the components of the triplet of the phenyl radical, $\Delta H = 45.0 \pm 1.5$ oersted, considerably exceeds the magnitude of the splitting on β-hydrogens in alkyl radicals (for example, in the radical $-CH_2 - \dot{C}H - CH_2-$, $\Delta H \simeq 30$ oersted ([3])). The large value of ΔH in benzene can be explained by the fact that the C–C distance in benzene is smaller than in aliphatic hydrocarbons, and that the orbital of the unpaired electron and the C–H bond of the phenyl radical lie in one plane.

As is seen from Fig. 1 (a, b, c), each component of the triplet is additionally split into 4 lines with $\delta H = 10.2 \pm 0.5$ oersted. This additional splitting can be assigned only to the interaction of the unpaired electron

with the three remaining H atoms. Such an interpretation of the spectrum makes it possible to conclude that these three hydrogen atoms are equivalent.

The low yield of molecular hydrogen ($G_{H2} = 0.036$ molecule/100 eV ([4])), in comparison with the polymer yield ($G_{poly} = 0.75$ molecule/100 eV ([5])) and with the radical yield according to our data (see Table 1), permits the conclusion that not all the hydrogen liberated in reaction (1) is evolved as H_2. This circumstance, as well as indications in the literature of the possibility of formation of the radical C_6H_7 from benzene and atomic hydrogen at liquid-air temperature ([6]), permits the conclusion that the greater part of the H atoms obtained in reaction (1) add to the benzene ring with formation of the radical C_6H_7. In the radical C_6H_7, the unpaired electron is delocalized in the π-system and interacts with many hydrogen atoms. By analogy with aromatic ion radicals ([7]), it may be assumed that the total magnitude of the hyperfine splitting in the radical C_6H_7 will be small (~ 20 Oe). Since in the solid phase the lines have a considerable width, the hyperfine-splitting components of the EPR spectrum of this radical will hardly be resolved. Therefore the spectrum of the radical C_6H_7 should be a single line of width 10–20 Oe.

Fig. 1. EPR spectra of irradiated samples: **a** –benzene at $-132°$; **b** –benzene at $-52°$; **c** –schematic representation of the benzene spectrum; **d** –diphenyl at $-124°$; **e** –*p*-terphenyl at $-124°$; **f** –*n*-ditolyl at $-124°$.

Fig. 2. Kinetics of radical accumulation at −124°: 1 −benzene, 2 −*p*-ditolyl, 3 −diphenyl, 4 −*p*-terphenyl

Figure 2: Fig. 2. Kinetics of radical accumulation at −124°: 1 −benzene, 2 −*p*-ditolyl, 3 −diphenyl, 4 −*p*-terphenyl

The superposition of this line on the central component of the phenyl-radical triplet makes it possible to explain completely all the features of the spectrum of irradiated benzene.

As is seen from Fig. 1a,b, the resolution of the hyperfine structure of the EPR spectrum of benzene improves with increasing temperature. It can be shown that this fact may be connected with the unfreezing of hindered rotation of benzene molecules about a sixth-order axis, the existence of which was shown in nuclear-resonance studies ([8]).

The spectra of diphenyl, terphenyls, and ditolyls are triplets similar to the benzene spectrum, but with poorer resolution of the individual components and without additional splitting of each of them. A characteristic feature of the spectra is their practically complete identity. All these features of the spectra can be satisfactorily explained by assuming that in polyphenyls detachment of an H atom or of a CH_3 group occurs in the *p*-position relative to the phenyl substituent. As a result of such detachment, radicals of the type

$$R-\overset{R'}{\underset{H}{}}$$

where $R' = CH_3$ in the case of *o*-ditolyl and $R' = H$ in the remaining cases. The detached H atom or CH_3 radical, adding to the benzene ring, gives a radical analo-

phenyl radical C_6H_7. The resulting spectrum will obviously be very close to the spectrum observed in the radiolysis of benzene. The worsening of the resolution of the structure of the spectra of polyphenyls is probably due to delocalization of the unpaired electron over the entire system of conjugated bonds, which should lead to its interaction with a large number of hydrogen atoms. In addition, in the case of polyphenyls there should be no line-narrowing mechanism associated with rotation.

Poor resolution of the e.p.r. spectra of polyphenyls could be associated with the possibility of formation of radicals of different types as a result of ruptures of different CH or C−C bonds. Such an assumption, however, does not allow one to explain the identity of the spectra of different polyphenyls.

Table 1 gives the radiation yields of radicals, determined from the linear portions of the accumulation curves (Fig. 2). The relative error in the determination of G_R is +20%.

Fig. 2. Kinetics of radical accumulation at −124°: 1 −benzene, 2 −*p*-ditolyl, 3 −diphenyl, 4 −*p*-terphenyl.

The decrease in the radiation yield of radicals in going from benzene to diphenyl and terphenyls agrees with the literature data on the increase in the radiation stability of polyphenyls in comparison with benzene ([9]). The larger yield of radicals in ditolyls in comparison with diphenyl apparently indicates a decrease in the radiation stability of the molecules upon introduction of side groups, which is in accordance with literature data ([10]). It is of interest to compare the radical yield in isomeric molecules. According to some literature data ([11,12]), terphenyl isomers at large irradiation doses differ substantially in their radiation stability; according to other data ([13]), where the yields of the final products of radiolysis were determined from the initial portions of the accumulation curves, this difference is small.

As is seen from Table 1, the difference in the value of G_R for the isomers apparently lies within the limits of experimental error.

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