EPR SPECTRA OF ANION-RADICALS OF CERTAIN AROMATIC HYDROCARBONS

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

UDC 547.024:538.113

PHYSICAL CHEMISTRY

**V. M. KAZAKOVA, B. I. SHAPIRO, I. G. MAKAROV,
Academician Ya. K. SYRKIN**

EPR SPECTRA OF ANION-RADICALS OF CERTAIN AROMATIC HYDROCARBONS

The literature describes the EPR spectra of anion-radicals formed upon the interaction of diphenylmethane and dibenzyl with metallic K in 1,2-dimethoxyethane [1]. These systems are of interest from the standpoint of the possibility of delocalization of the unpaired electron in phenyl rings separated by methylene groups. Since the spectra described do not make it possible to solve this problem unambiguously, we undertook additional studies of the EPR spectra of anion-radicals formed from such hydrocarbons under various conditions and at different temperatures, in order to study the processes occurring in these systems.

The anion-radicals were obtained by us in a special apparatus, which made it possible to introduce metallic K into a $5 \cdot 10^{-2}$ M solution of the hydrocarbon in

Table 1

Substance	Solvent	Temp., °C	Splitting pattern	Splitting constants, oersted
1. Diphenylmethanea) blue solutionb) green solutionc) reddish-brown solution	DMEKTHF	$-90 \div -80 -80 \div -70$room	5(3 × 5 × 5)3 × 5 × 5	$a_1 =$ 4.5($a_1 =$ 5.5; $a_2 =$ 4.4; $a_3 =$ 2.2)$a_1 =$ 5.2; $a_2 =$ 2.6; $a_3 = 0.4$
2. Diphenylethane	DME	$-80 \div -70$	5 × 4	$a_1 =$ 4.9; $a_2 = 1.0$
3. 1,3-Diphenylpropane	DME	$-80 \div -70$	5 × 4	$a_1 =$ 5.0; $a_2 = 0.9$

Fig. 1. EPR spectra of the anion-radicals of diphenylmethane in 1,2-dimethoxyethane at −90° (I) and diphenylethane in 1,2-dimethoxyethane at −80° (II)

Figure 1: Fig. 1. EPR spectra of the anion-radicals of diphenylmethane in 1,2-dimethoxyethane at −90° (I) and diphenylethane in 1,2-dimethoxyethane at −80° (II)

1,2-dimethoxyethane or tetrahydrofuran after removal of oxygen from the system by repeated freezing and thawing of the solution at a residual pressure of 10^{-3} mm Hg. The anion-radicals were then accumulated in solution by the generally accepted procedure, and part of the solution was withdrawn through a spider into an ampoule and annealed in the frozen state. Samples were taken at different time intervals, beginning with the first, when a coloration appeared that was stable for several minutes. The last sample was taken after several days, when the solution remained colored even at room temperature.

The EPR spectra were recorded on a standard RE-1301 radiospectrometer at a temperature in the resonator from −90° to room temperature. Diphenylmethane and diphenylethane of "highest purity" grade were additionally recrystallized from alcohol before use. 1,3-Diphenylpropane was synthesized and purified according to the method described in [2]. The solvents used, 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF), were thoroughly purified by standard methods.

The EPR spectra obtained are shown in Figs. 1–3; the principal characteristics of the spectra are summarized in Table 1.

In all the cases we studied, the solutions of the initially formed anion-radicals have a blue or blue-green color and give

EPR spectra consisting of the main quintet with a component intensity ratio of $1:4:6:4:1$ (Fig. 1). The character and splitting constants of the spectra definitely show that in the anion-radicals that are the primary reduction products of the hydrocarbons studied with metallic potassium, the unpaired electron is delocalized only in one phenyl ring. The quintet arises from the interaction of the unpaired electron with four equivalent ortho- and meta-protons of the ring, as in toluene. It should be noted here that the splitting constants a_1 are also close in magnitude to a_1 in toluene (3), especially for the anion-radicals of 1,2-diphenylethane and 1,3-diphenylpropane. For these compounds, the initially formed primary anion-radicals are unstable and decompose when the temperature is raised above −70°.

Fig. 1. EPR spectra of the anion-radicals of diphenylmethane in 1,2-dimethoxyethane at −90° (I) and diphenylethane in 1,2-dimethoxyethane at −80° (II)

The quintet spectrum of the diphenylmethane anion-radical already at −80°

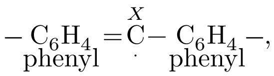
Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

changes into a well-resolved spectrum consisting of 23 components of hyperfine structure (h.f.s.). The number of components and the intensity ratio agree satisfactorily with the theoretical values, which correspond to a splitting pattern of $3 \times 5 \times 5$ and to the ratio of splitting constants $a_1 : a_2 : a_3 = 2.5 : 2 : 1$. This spectrum already belongs to an ion-radical in which the electron is delocalized in at least two phenyl rings, since in one phenyl ring there are not enough protons to give rise to the observed h.f.s. It is quite probable that this ion-radical, which is relatively stable at −70°, is a paramagnetic dianion of the general formula



$$-\underset{\text{phenyl}}{C_6H_4}=\overset{X}{\underset{\cdot}{C}}-\underset{\text{phenyl}}{C_6H_4}-, \quad \text{where } X = \text{H or K.}$$

It is known from the literature that the hydrogens of a methylene bridge are fairly mobile and that the metalation reaction is possible under the experimental conditions, all the more so because only a small percent yield—from 1 to 5 —is sufficient to produce the effect. Solvation in a polar solvent should also contribute to stabilization of the dianion.

The assumption of the existence of a dianion-radical is supported by the fact that, for diphenylethane and diphenylpropane, we did not observe similar radicals in which the phenyl rings would be conjugated. This is possibly connected with the fact that, in these cases, formation of a conjugated system would require the removal of several protons from different carbon atoms, which is apparently unlikely.

When an attempt was made to obtain the anion-radical of diphenylmethane at high concentrations, the color of the solution changed to reddish-brown and did not disappear even at room temperature. The EPR spectrum consists of 9 hfs lines with further splitting of each into 5 components (Fig. 3). Analysis of the spectrum showed that it possibly belongs to the diphenyl anion-radical, whose spectrum is described in papers (4, 5). The nine lines arise from a triplet split into a quintet, with a ratio of splitting constants of 2 : 1 (the ratio of line intensities within the nonet is 1 : 4 : 8 : 12 : 14 : 12 : 8 : 4 : 1). Thus, it is evident that the radical products of the reduction of diphenylmethane are unstable and over time transform into the more stable diphenyl anion-radical, which also exists at room temperature.

Fig. 2. EPR spectrum of the radical formed from diphenylmethane in 1,2-dimethoxyethane at −75°

Fig. 3. EPR spectrum of the anion-radical formed from diphenylmethane at room temperature

In conclusion, it should be noted that the EPR spectra consisting of 9 principal lines, which were assigned by the author (1) to the anion-radicals of diphenylmethane and diphenylethane, actually belong to the anion-radicals of compounds that are products of decomposition of the starting hydrocarbons.

We are continuing to study these systems and hope in the near future to elucidate the structure of the secondary paramagnetic products formed in the interaction of diphenylmethane and dibenzyl with metallic potassium.

Moscow Institute of Fine Chemical Technology
named after M. V. Lomonosov

Received
6 VII 1965

CITED LITERATURE

1. S. P. Solodovnikov, *Zhurn. struktur. khim.* **2**, 282 (1961).
2. M. Konovalov, S. Dobrovol' skii, *ZhRFKhO*, **37**, 548 (1905).
3. J. R. Bolton, A. Carrington, *Mol. Phys.*, **4**, 497 (1961).
4. E. De Boer, *J. Chem. Phys.*, **25**, 190 (1956).
5. M. G. Townsend, *J. Chem. Soc.*, 1962, No. 1, 53.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.