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UNPAIRED ELECTRON DELOCALIZATION IN DIARYLMETHANE ANION-RADICALS

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The problem of the unpaired electron exchange frequency in the α,ω-diarylalkane anion-radicals has remained unsolved in spite of a considerable amount of experimental (I-5) and theoretical (6, 7) work. Until now a possible exchange reaction (8) between the anion-radical and non-radical components of the system has not been taken into consideration. This delocalization mechanism can compete with the unpaired electron transfer through the barrier of the bridge group.

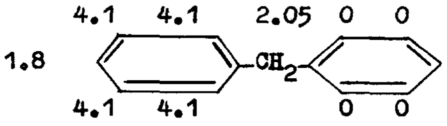
We have investigated the ESR spectra of the anion-radicals of diphenylmethane (I-K), α,α'-dinaphthylmethane (II-K), and α,α'-I,2-dinaphthylethane (III-K). Fig. I shows the ESR spectrum of the anion-radical I-K in I,2-dimethoxyethane (DME) with potassium at -70°, and Fig. 2 gives the spectrum of the same anion-radical in a mixture of I,2-dimethoxyethane-tetrahydrofuran (THF) (I:I) at -100°. As the temperature increases up to -70° the spectrum in Fig. 2 reversibly turns into the spectrum given in Fig. I. Analysis of the spectra shown in Figs I and 2 results in the following hyperfine splittings

$$a_{ortho} = a_{meta} = a_{CH_2} = 2.05\ G,\ a_{para} = 0.9\ G\ (5).$$

The changes observed in the solvent mixture are connected with the hyperfine line width alternation due to abnormal broadening of the odd components (9-II). This broadening $\Delta\,(T_2^{-I})$ is described by the following expression (IO):

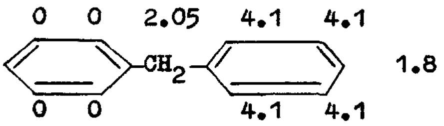
$$\Delta\,(T_2^{-I}) = \frac{\gamma_e^2 (a_I - a_{II})^2\ (M_I - M_{II})^2}{2\nu_{exc}}\ ,$$

where ν_{exc} is the electron exchange frequency from one phenyl ring to the other one; M_I and M_{II} are the magnetic quantum numbers for the total Z components of the nuclear angular moments of the protons in the first and second phenyl rings; a_I and a_{II} are the hyperfine splittings of forms I and II; γ_e is the magnetogyric ratio of the electron.



I

and



II

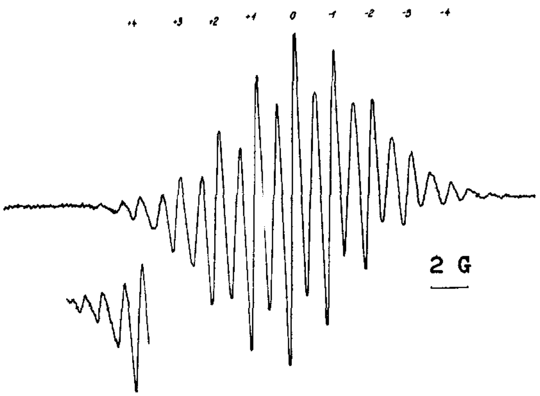


Fig. I. The ESR spectrum of diphenylmethane anion-radical in DME at -70°

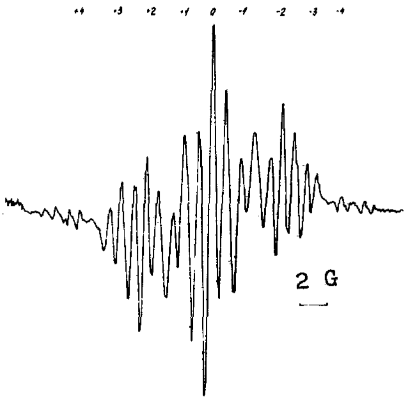


Fig.2. The ESR spectrum of diphenylmethane anion-radical in the mixture of DME-THF (I:I) at -100°

The lines corresponding to the projections of the ortho- and meta-proton magnetic moments will undergo the greatest alternation since their value of $(a_I - a_{II})^2 = (4.IG - 0)^2 = I6.8I\ G^2$ is considerably higher than for para-protons, which is $(a_I - a_{II})^2 = (I.8\ G - 0)^2 = 3.24\ G^2$. The hyperfine lines of methylene protons will not be affected by the electron exchange due to symmetry. The line intensities in groups M = 0 and M = ±2 in Fig. 2 have the following relation: I:2:3:4:3:2:I, which is connected with the value of $a_{CH_2} \approx 2a_{para}$. The line width is smaller in groups M = ±4 and the splittings a_{para} and a_{CH_2} are clearly distinguished. The preliminary value of the exchange frequency is $\nu_{exc} = 3 \cdot 10^{13} \exp(-4000/RT)\ sec^{-1}$.

A similar picture is observed in the ESR spectra of the anion-radicals II-K. A qualitative analysis shows that the ESR spectrum of the anion-radical II-K in THF coincides with that of the anion-radical III-K in DME. On the basis of this result and the data given in ref. (2-5) it is possible to make a conclusion that the exchange frequency is small in the anion-radical II-K as compared with the hyperfine splittings. The ESR spectrum of the anion-radical II-K in DME differs from that in THF both by the smaller values of the splittings and the smaller total width of the spectrum. Interesting changes take place with temperature in the ESR spectrum of II-K in the DME-THF mixture (I:I). The spectrum coincides with that in DME at -70° and at -115° it is similar to the spectrum in THF at -110°.

The behaviour of the I-K and II-K anion-radical spectra in pure DME differ sharply from that in the mixture with THF. Uniform broadening of all the spectrum components is observed when the temperature decreases to the DME freezing point and below.

Thus, the unpaired electron in I-K and II-K is completely delocalized in DME, an intermediate picture (from the unpaired electron delocalization towards its localization) is observed in the mixture with THF depending on temperature, and the unpaired electron is localized in one part of molecule II-K in THF.

We believe that the main cause of a different character of the spectra in DME and THF as well as in their mixture is connected with the different nature of the ion pairs, which is known to affect strongly the exchange rate constants in these solvents (8, I2).

The loose ion pairs in DME are more active in the electron exchange reactions as compared with the contact ion pairs in THF. As is known (I3), electron exchange is connected with a synchronous metal cation transfer from one molecule to another and therefore it is a different mobility of the potassium cation in DME and THF, which determines the different delocalization frequen-

cies in these solvents. The results obtained may have general significance for understanding delocalization in systems (Ar - X - Ar) $^{\overline{\cdot}}M^{+}$.

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