

## CONTRIBUTION TO THE EPR-SPECTRA OF MOLECULAR COMPLEXES: THE SYSTEM TRIPHENYLPHOSPHINE-TETRACYANOETHYLENE IN DICHLOROETHANE

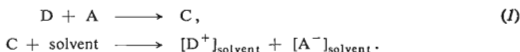
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Measurements of absorption and EPR-spectra of the system triphenylphosphine-tetracyanoethylene confirmed the formation of  $[\text{TCNE}^-]$ . The influence of the mutual ratio donor-acceptor on the shape of the EPR-spectra was investigated; the disappearance of the spectrum of one species is explained to be due to a rapid charge transfer.

Mutual interaction of molecules exhibiting donor and acceptor properties leads to the formation of a molecular complex characterized by a new absorption band in the visible or the ultraviolet region of the spectrum. Both the interaction and charge transfer increase with the decreasing ionization potential of the donor and with the increasing electron affinity of the acceptor<sup>1</sup>. In an interaction of a strong donor with a strong acceptor the contribution of the dative structure of the complex is significant. By the dative structure we understand a complex structure arising from a partial or a complete charge transfer from the donor to the acceptor. If such an interaction takes place in a solvent of sufficiently high dielectric constant, dissociation of the complex and formation of ion pairs occurs:



In reality this process may not be necessarily so simple, but may proceed in several steps. The formation of an excited triplet and its subsequent dissociation was considered<sup>2,3</sup>. Similarly,  $[\text{D}^+]$  and  $[\text{A}^-]$  may not be simple ions of the original neutral molecules. The final products of these processes are molecular systems with an open electron shell-radical ions. These systems can be conveniently studied by means of the electron paramagnetic resonance (EPR) method. It is an interesting fact that most EPR-spectra of the molecular complexes so far measured have shown a spectrum of only one species of the radical ion of the system.

We report in this communication on our study of the interaction tetracyanoethylene (TCNE) – triphenylphosphine (TPP). Tetracyanoethylene is a strong  $\pi$ -type acceptor whose lowest unoccupied molecular orbitals are of the bonding type. Triphenylphosphine is a strong  $n$ -type donor (non-bonding lone pair).

## EXPERIMENTAL

The substances used in this study, TCNE, TPP, and dichloroethane, were commercial products of Lachema, purified in the laboratory by usual procedures. The molecular complex was prepared in all cases by simple mixing the donor and the acceptor solution. The preparation of the complex and the measurements were carried out at the laboratory temperature in the presence of air. Absorption spectra were recorded on a Specord-UV VIS instrument employing quartz cells. EPR spectra were measured using either a ER 9 spectrometer or the EPR-instrument constructed and operated at the School of Experimental Physics of the Comenius University.

## RESULTS AND DISCUSSION

The EPR-spectrum in Fig. 1 is a nine-line symmetric spectrum with a resolved hyperfine splitting. The lines in the spectrum have the following intensity ratios: 1 : 4 : 10 : 16 : 19 : 16 : 10 : 4 : 1. This corresponds to an interaction of an unpaired electron with four equivalent nuclei whose nuclear magnetic moment is  $M_I = 1$ . In our system this spectrum corresponds to the radical-anion  $[\text{TCNE}^-]$ . The splitting is

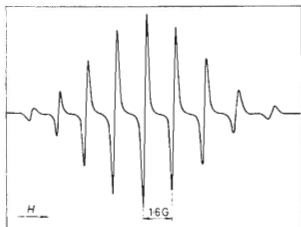


FIG. 1

EPR Spectrum of the System TPP-TCNE (2 : 1) in Dichloroethane

$1 \cdot 10^{-3}$  mol TPP and  $5 \cdot 10^{-4}$  mol TCNE dissolved in 3 ml of the solvent; modulation 0.01 G;  $g$ -factor of the central line 2.0036.

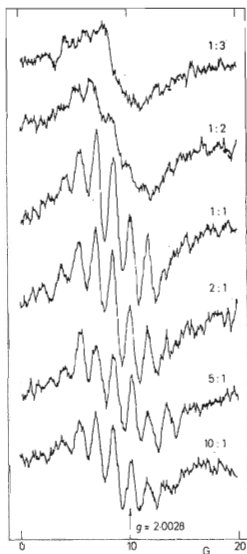


FIG. 2

EPR Spectra of the System TPP-TCNE in Dichloroethane at Various Molar Ratios D : A

Initial concentrations of both donor and acceptor were  $5 \cdot 10^{-2}$  M; modulation 0.2 G.

caused by the four equivalent nuclei of the  $^{14}\text{N}$  isotope. The splitting width between the lines of the spectrum is 1.6 G. Similarly, the splitting about 1.6 G exhibits both the spectrum of the radical anion  $[\text{TCNE}^-]$  as published in the Atlas of ESR Spectra<sup>4</sup> and the spectrum of  $[\text{TCNE}^-]$  prepared in our laboratory by reduction by the sodium mirror. In the studies of strong molecular complexes of tetracyanoethylene with various donors<sup>2,3,5-7</sup> the signal of the radical anion  $[\text{TCNE}^-]$  was recorded. However, in none of these studies a signal of the radical cation was registered. It is necessary to note that these systems contained an excess of the donor. The same was true also for our system which yielded the spectrum in Fig. 1.

The influence of the ratio donor to acceptor can be seen in Fig. 2. Indeed, the spectrum with the resolved hyperfine splitting obtains in the molar excess of the donor. In the opposite case, the hyperfine splitting in the spectrum of  $[\text{TCNE}^-]$  collapses. A similar effect was described<sup>8</sup> in the system fluoranil and NaI. The interesting feature of the spectra in Fig. 2 is that the spectrum is superimposed. The spectra in this figure were obtained with the limiting sensitivity of the instrument with a modulation of about 0.2 G. For that reason, the individual lines of the spectrum are overmodulated (halfwidth of a line is about 0.3 G). However, the whole spectrum cannot be overmodulated and thus the broad simple line could not arise as a result of the overmodulation. The simple line in this spectrum can be assigned to the radical cation in this system. Similarly, in the investigation<sup>9,10</sup> of complexes of chloranil with N,N,N',N'-tetramethyl-*p*-phenyldiamine the ESR-spectrum of both radical ions present in the solution was recorded.

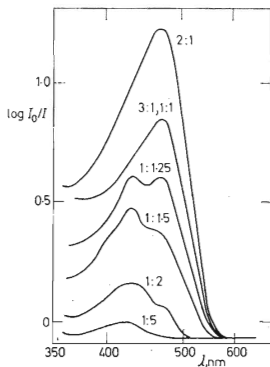
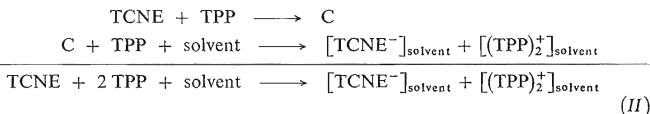


FIG. 3  
Absorption Spectra of the System TPP-  
-TCNE in Dichloroethane at Various Molar  
Ratios D : A

Initial concentrations of both components  
 $5 \cdot 10^{-2} \text{ M}$ .

The absorption spectrum of the system studied (Fig. 3) exhibits the absorbance at two different wavelengths. Let us note here that none of the interacting components itself absorbs in this region. The change of the absorbance at 470 nm and 425 nm with the changing ratio D : A indicates the absorption of two components in the system. The absorption band peaking at 470 nm belongs to the radical<sup>11</sup> anion [TCNE<sup>-</sup>]. In the molar excess of the acceptor the maximum absorbance occurs at 425 nm, and this absorption band can be assigned to the radical cation. Evaluation of the absorption spectra at 470 nm by means of the Job method gave the ratio D : A = 2 : 1.

On the basis of the measured data we may assume the following course of the donor-acceptor interaction



The collaps of the hyperfine structure of the spectrum of [TCNE<sup>-</sup>] (Fig. 2) in the molar excess of the acceptor may be then explained as a rapid electron exchange between the ion and the neutral molecule TCNE; this leads to a broadening of the spectrum up to the point that it cannot be registered. In the molar excess of the donor and at high concentrations the transfer of a "hole" between the donor cation and its neutral molecule occurs in a similar way. As a result, the EPR-signal of the donor becomes non-registrable.

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