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THE INVESTIGATION OF PHOTOCONDUCTIVITY AND MAGNETIC FIELD EFFECT IN 1,4-DIAMINO ANTHRAQUINONE

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Abstract The steady-state photoconductivity of 1,4-diamino anthraquinone dye and its variations in external magnetic field in the temperature range 213-313 K have been measured. The results may be regarded as proof of participation of the different types of the pairs of paramagnetic particles in charge carrier generation process.

INTRODUCTION

Di-substituted derivative of anthraquinone, namely, 1,4-diamino anthraquinon (DAAQ) is of commercial importance as a disperse dye and has a variety of applications including such fields as a textile industry, electrophotography and liquid crystal display devices. Its light fastness on textile fibers and other photophysical properties are not clear fully in spite of several works have been undertaken to study them.[1] Steady-state photoconductivity in thin films of the series of anthraquinone derivatives have been also measured and some peculiarities of the charge generation process have been established.[2] In this work we tried to define more precisely the details of the processes of charge carrier photogeneration and recombination in thin films of 1,4-DAAQ measuring the steady-state photoconductivity and its variations in external magnetic field (magnetic field effects (MFE) method[3]).

EXPERIMENTAL

Commercial (97% pure) 1,4-DAAQ was purified at first by Soxhelet extraction technique with pure ethanol (99,99% pure). Further it was purified by repeated recrystallization from purified ethanol, then by column chromatography over activated silica gel (special for column chromatography, BDH, London) using pure ethyl acetate and chloroform mixture (1:1) as the eluent, zone refining and finally by vacuum sublimation.

The absorption spectra of thin films of the dye evaporated on the quartz substrate have been recorded on Specord M-40 spectrophotometer.

The electrical measurements have been carried out on surface-type cells in vacuum 10^{-5} Torr within the temperature range 213-313 K. The thickness of the dye evaporated on quartz substrate with Al electrodes was few tens of μm. The electrical field strength did not exceed 30 kV/cm. Magnetic field value was varied within 0-12 kOe. The maximum intensity of the unfiltered white light from the filament lamp on the sample was 140 Wt/m^2.

RESULTS AND DISCUSSION

Photocurrent spectrum showed two peak values at 385 nm and at 661 nm and was antibatic to the spectrum of absorption. It may be explained by intensive surface recombination of charge carriers, that leads to decreasing of their steady-state concentration. Under the action of oxygen there was a marked decrease (of about 60%) of the photocurrent value. Most probably the adsorbed oxygen molecules act as traps for electrons that are main charge carriers.

The dependence of photocurrent value i_{ph} on intensity of light I looked as $i_{ph} \sim I^m$. In the case of illumination with monochromatic light of wavelength 366 nm or 625 nm (the intensity range being $4{,}7 \cdot 10^{-4}$ to 10^{-1} Wt/m^2) a transition was observed from $m \approx 1$ at intensities below $1{,}3 \cdot 10^{-3}$ Wt/m^2 to $m \approx 0.5$ at higher intensities. The value

of m increased with decreasing of the temperature in the higher intensity range. In the case of illumination by unfiltered white light $m = 0.61 \mp 0.06$ (the intensity range was 0.6 - 140 Wt/m^2) and practically did not depend on temperature. Such dependences of the photocurrent on light intensity reflect the presence of traps in the sample that acts as the centres of recombination. But the nature of the traps is not clear completely. Maybe they are the traces of anthracene. In particular the existence of shallow traps is confirmed by the temperature dependence of the charge carrier mobility[2] $\mu \sim T^{-1,1}$ reflecting their multiple capture.

The temperature dependence of i_{ph} is shown on Fig.1. A knee is observed in the region of 250 K irrespective of exciting light wavelength. The activation energy was ~ 0.14 eV below 250 K and ~ 0.04 eV above 250 K. Such unusual behaviour may be understood if to suppose that this dependence reflects as the activation character of the charge carrier generation process and the decreasing of their mobility with increasing of the temperature according to above mentioned law.

One of the features of organic solids with low

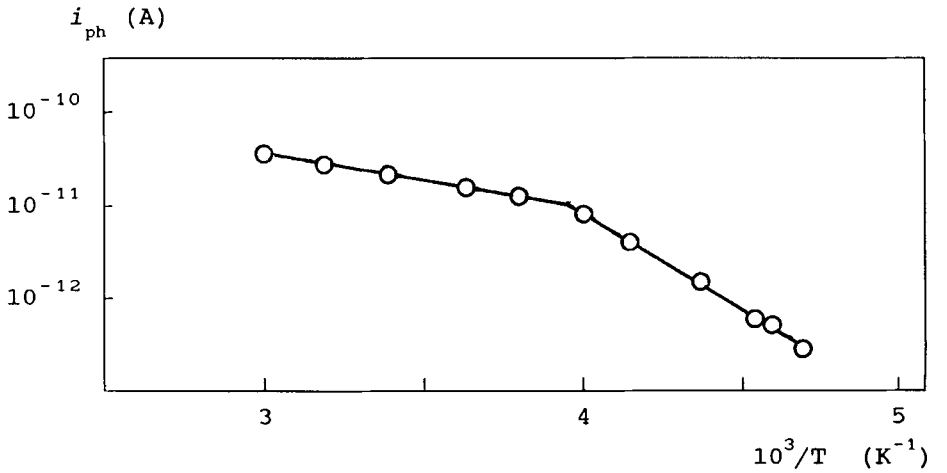

FIGURE 1 Photocurrent vs temperature dependence. Excitation by light with wavelength λ=620 nm.

mobility of charge carriers is the specific influence of magnetic field on their photoconductivity. In such systems the photoexcitation leads at first to the formation of correlated electron-hole pairs. This pairs may recombine or dissociate forming free charge carriers. The influence of magnetic field on the photoconductivity is the consequence of dependence of the recombination rate on the pair spin state.[3] As a rule their primary state is singlet one but it is changing during the lifetime of the pair and becomes singlet-triplet mixture. The external magnetic field changes the rate of such intersystem crossing and consequently affects free charge carriers concentration that is proportional to the total population of singlet and triplet states.

In our case the photoconductivity of DAAQ increased on the application of the external magnetic field. The relative change dependence of the photocurrent value (MFE), $\Delta i_{ph}/i_{ph} = [i_{ph}(H)-i_{ph}(0)]/i_{ph}(0)$, on the magnetic field strength had a form of a curve with saturation that

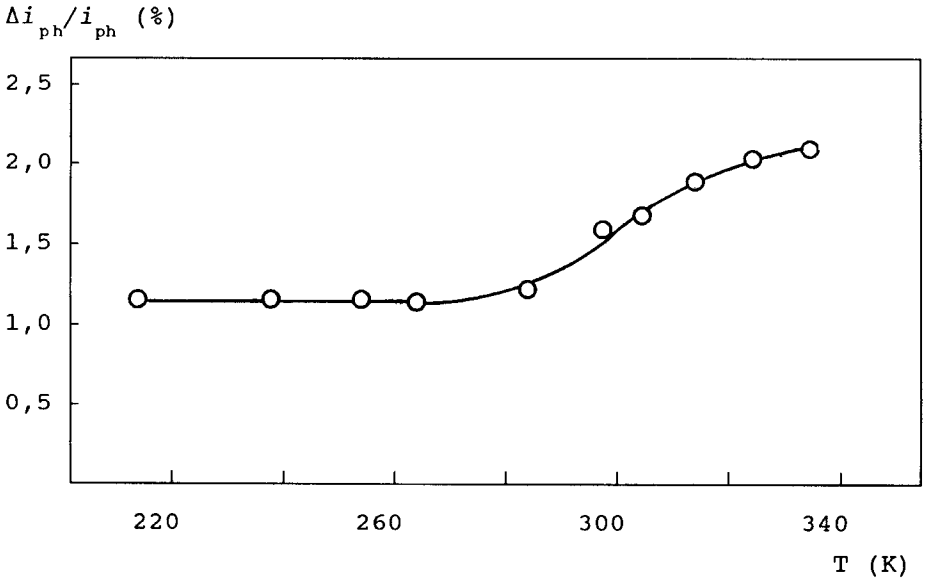

FIGURE 2 MFE dependence on temperature (H=10 kOe). Excitation by white light.

corresponds to the hyperfine interaction (HFI) mechanism of mixing of the singlet and triplet states of electron-hole pairs. Half of the maximum value of MFE was obtained in the field $H_{1/2}$= 60-100 Oe. MFE value did not depend on the exciting light wavelength in the range 366-825 nm. Lowering of the temperature led to decreasing of the MFE value but below 250 K it remained constant (Figure 2).

The character of the MFE dependence on magnetic field strength did not change with changing of the temperature.

As have been shown recently[4] the temperature dependence of MFE is defined by the difference of the energies of the electron-hole pair state where the exchange interaction essentially exceed HFI value and the state where the exchange interaction practically equals to zero. It is connected with the fact that mixing of the singlet and triplet states of electron-hole pairs takes place at the distances where the exchange interaction is absent and checking of the spin is carried out during the short approach up to distances where the exchange interaction is large. As a rule MFE value monotonically decreases up to zero with the lowering of the temperature.[4] The feature of the result received in this work consists in the constant value of MFE below 250 K. We suppose that at least two types of pairs of particles with the spin 1/2 take part in the photogeneration process and contribute to the observable MFE value.

The another result that may be regarded as the argument in favour of this hypothesis is the dependence of MFE value on intensity of the exciting light (Figure 3). It is well known that excitation of the organic solids by the light of low intensity leads to creation of geminate electron-hole pairs in singlet state as a rule. With increasing of the light intensity the electron-hole pairs of the same kind but in all possible spin states may be created during the meeting of the free charge carriers of opposite signs. In such regime MFE value starts to decrease. If only one type of electron-hole pairs is formed then in the limit case when pure bimolecular recombination

operates, MFE must be approximately two times less of its value at low intensity.[4] We were able to receive the MFE dependence on intensity only for white light. It is seen that MFE decreases more than three times with the changing of light intensity from 0.6 to 140 Wt/m^2 although the bimolecular recombination operates in whole range. Such a decrease may be caused by recombination of free charges with ones belonging to geminate pairs. The process suggested would equalize the lifetimes of singlet and triplet pairs.

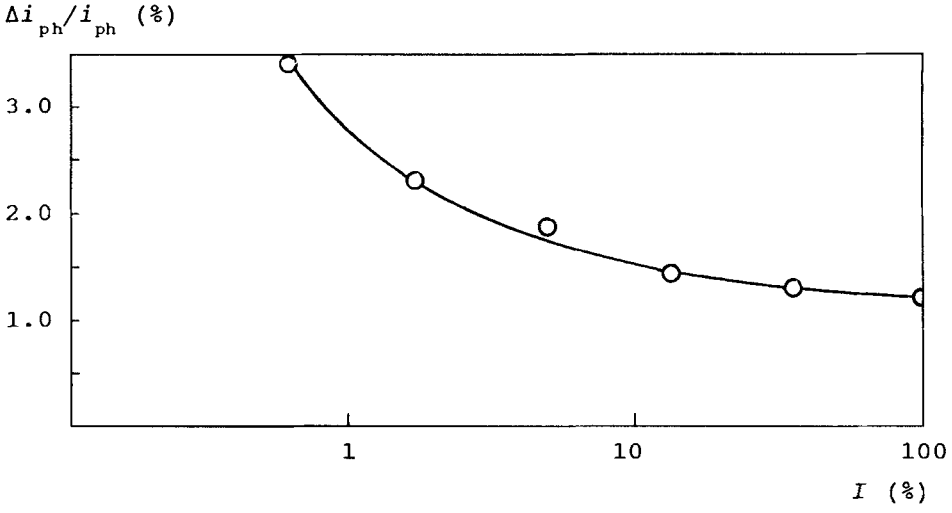

FIGURE 3 The MFE dependence on intensity of exciting white light, T=295 K.

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