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Abstract

Full Text

Physical Chemistry

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Formation of Paramagnetic Centers and EMF during Electrochemical Reactions in Polycrystals of Triphenylmethane Dyes

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In a previous communication [1] it was shown that, in polycrystalline samples of the dye brilliant green, illumination with light from an incandescent lamp gives rise to electron-paramagnetic-resonance signals (EPR), which, unlike those of a number of other dyes, are absent in the unilluminated sample. A similar effect for brilliant green was found in [2]. We have found that the photoinduced paramagnetic centers responsible for the "narrow" EPR signal ($\Delta H_{1/2} = 2.7$ oersted) are thermally activated. Their number changes reversibly with temperature according to the law $N = N_0 \exp(-\Delta E/kT)$, where $\Delta E = 0.1$-0.15 eV. At elevated temperatures the signal disappears irreversibly. Similar photoinduced signals were also observed in dye films [3]; however, the lifetime of the paramagnetic centers in this case is extremely short, and they can be observed only under continuous illumination.

In the present work we describe several new electrical and magnetic effects observed when an electric current passes through pressed tablets of polycrystalline samples of brilliant green [1]. Analogous phenomena were also found for other dyes (II–VI).

[Structural formula V]

[Structural formula VII]

I–VI were industrial samples subjected to repeated recrystallization from water and alcohol. Within the experimental error, we found no effect of recrystalliza-

tion on the observed phenomena. Dye VII was synthesized by the Grignard reaction from Michler' s ketone and contains inorganic impurities in an amount less than $2 \cdot 10^{-4}$%. All experiments described below were carried out on dye I and are valid for II–VII.

Tablets were obtained by pressing the powder at pressures up to 6000 kg/cm^2. Electrodes made of tin, copper, aluminum foil, or graphite were pressed into the tablet during pressing. The electrode material did not affect the electrical and magnetic properties of the samples. The conductivity of the tablets was studied using a conventional electrometric circuit in fields up to 2500 V/cm at temperatures of 0—50°C in air and on samples trained in vacuum.

[Figure 1 graph]

Fig. 1. Decay of the emf of a tablet of dye I after charging

Positive deviations from Ohm' s law were found. At constant voltage the conductivity increased with time. This effect is clearly noticeable even in fields of 50 V/cm and increases strongly with increasing field strength. The increase in conductivity with time can lead to breakdown of the tablet after several hours even in fields below 100 V/cm. The current-voltage characteristic had a region of negative resistance, passing into breakdown. The conductivity depends on temperature according to the law $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, where $\Delta E = 2.1$ eV (the value of ΔE was obtained by extrapolation to zero field strength). At room temperature and a field strength of 360 V/cm, the conductivity of the tablets is of the order of 10^{-8} $\Omega^{-1} \cdot \text{cm}^{-1}$.

[Figure 2 graph]

Fig. 2. Increase and decrease of the intensity of the EPR signal of a tablet of dye I in successive discharge and charge cycles. The arrows indicate the beginning of discharge (↓) and the beginning of charge (↑)

The flow of current through the tablet leads to the appearance in it of a potential difference of the same sign as the applied voltage. In essence, this is the appearance of an electromotive force, the charging of the tablet, reminiscent of the charging of an accumulator.

The rate of decay of the emf of the tablet does not depend on the magnitude of the external resistance. Even a short circuit does not lead to its increase. The emf on the tablets increases with increasing voltage during charging, reaching at

best samples, 75 V at a charging voltage of 300 V and a tablet thickness of 0.15 cm. Usually we worked with lower voltages and initial emf values of about 3 V. As is seen from Fig. 1, the emf of the tablet decreases with time. In the best samples the decrease of the emf to a value of 0.1 V at room temperature continues for 48-56 h (dye III). As the temperature rises, the rate of decrease increases. An estimate of the efficiency from the electrical energy expended and obtained during discharge gives a value of 1-1.5%.

It is known that, during the electrolysis of solutions of triphenylmethane dyes, neutral free-radical compounds are liberated at the cathode, representing products of electron addition to the dye cation ([4]). We assumed that analogous processes may occur in the solid phase. Indeed, passing a current through a tablet leads to the appearance of a singlet EPR signal with a g-factor practically coinciding with the purely spin value and with a width $\Delta H_{1/2} = 1.5$ Oe.

The EPR signal rises and falls in parallel with the magnitude of the tablet emf during charge-discharge processes, which can be carried out repeatedly. Fig. 2 gives a typical curve of the increase and decrease of the EPR signal for several cycles. Samples taken in the cathodic and anodic regions of the tablet showed that the paramagnetic centers responsible for the observed EPR signals are concentrated near the cathode. Raising the temperature leads to a sharp increase in the rate of disappearance of the EPR signal during discharge. In this connection the temperature dependence of the EPR signal was investigated from 300 to 77°K. It was found that the signal intensity does not obey Curie' s law, while the number of paramagnetic centers changes according to the law $N = N_0 \exp(-\Delta E/kT)$, where $\Delta E = 0.1$-0.2 eV, which practically coincides with the temperature dependence of the "narrow" light-induced EPR signal in the same samples. Neutral dyes of the bromindigo type do not possess such properties.

It may be supposed that, in the process of electrochemical reduction in the solid, the reaction $K^+ + e \rightarrow K^0$ proceeds with the formation of a neutral free radical of the dye. A similar process probably also occurs with anions. The process reverse to electrolysis leads to the appearance of an emf.

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