

Temperature Dependence of Sensitized Photocurrents between 200 and 293 K

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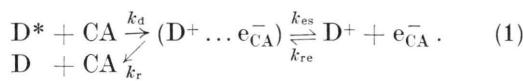
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With an oxacarbocyanine dye monolayer on the surface of a p-chloranil single crystal and sandwiched between metal electrodes the temperature dependence of sensitized photocurrents has been measured with this “dry” electrochemical cell in the temperature range from 200–293 K. The activation energy of 0.26 ± 0.02 eV is discussed in terms of a reaction scheme that involves a thermalization distance within the coulomb well of an intermediate state.

1. Introduction

The kinetics of sensitized charge carrier injection from excited dyes into molecular crystals is now rather well understood with respect to the energetic requirements at the phase boundary [1]. Furthermore, the dependence on the electric field [2] as well as the dependence of a quantum efficiency on a magnetic field [3] suggests that an intermediate “charge-transfer state” ($D^+ \dots e^-_{CA}$) is involved in a reaction scheme that describes the charge carrier injection from an excited dye molecule D^* into the chloranil crystal CA with rate constant k_d and yields finally with rate constant k_{es} an ionized dye molecule D^+ at the phase boundary and an electron e^-_{CA} within the chloranil crystal,



The rate constants for recombination are k_r and k_{re} , respectively. The dissoziation of $(D^+ \dots e^-_{CA})$ should be possible by the diffusional motion of the charge carriers in the crystal over a potential barrier that is formed by the superposition of the coulombic attraction potential and an externally applied field.

The temperature dependence of the sensitized photocurrent and the determination of an activation energy should give more information about the charge carrier injection across the phase boundary and the diffusional escape from the coulomb well. But, unfortunately, the use of aqueous dye solutions in contact with molecular crystals is not a very suitable experimental arrangement. Apart from the fact that the temperature range is limited because of either freezing or

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evaporation of the droplet, temperature dependent adsorption phenomena are involved in the photocurrent density. At least it has been found from photocurrent measurements in a limited temperature range of 30 K, that activation energies depend on the concentration of the dye in solution [4].

The use of dye molecules in a monolayer assembly on the surface of molecular crystals precludes adsorption phenomena. Those “dry” electrochemical cells with evaporated aluminum electrodes [5] al/arachidic acid, dye monolayers/crystal/al, where additional arachidic acid monolayers between the dye and the electrode prevent the quenching of the dye’s excitation energy, are the suitable arrangement for the storage in vacuum and cooling down to temperatures below 293 K.

The present paper reports about the temperature dependence between 200 K and 293 K of sensitized photocurrents that are obtained by exciting an oxacarbocyanine dye on the surface of p-chloranil single crystals. From heating curves under steady state illumination an activation energy of 0.26 eV could be determined. It is discussed in terms of the reaction scheme above and of a thermalization distance within the coulomb well.

2. Experimental

Single crystals of p-chloranil with (*a*, *b*) surfaces have been grown by sublimation. Afterwards, with flakes of about 0.5 cm^2 sandwich cells were built: at first an electrode of aluminum with 4 mm diameter was evaporated onto one surface of the crystal, then a mixed dye monolayer of the stearyl-substituted dye oxacarbocyanine chlorate and arachidic acid was deposited by the monolayer technique [6]. Additional 4–6 monolayers pre-



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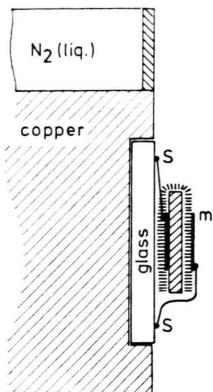


Fig. 1. Sandwich cell (monolayers exaggerated) mounted on a glass slide that is in thermal contact with a sample holder of copper.

vented the quenching of excitation energy at the second aluminum electrode (m1 in Fig. 1) that was evaporated afterwards. During evaporation in vacuum the probes were placed on a mask that was cooled by liquid nitrogen, and the transparency of the electrodes of typical 25% was controlled by an optical detector.

A cryostat has been constructed that allowed for electrical measurements and for optical excitation of the sandwich cells through glass windows. It could be evacuated with an oil diffusion pump down to 10^{-5} bar, and cooling down to 77 K was possible by pouring liquid nitrogen into a vessel that was connected with a sample holder made of copper (Figure 1). The latter contained a heating resistor and a groove, where a glass slide of size 1×2 cm could be brought in thermal contact with grease. A copper/constantane thermo-couple was fixed with silver paste onto the glass slide to measure the temperature.

With the directly metal covered surface, the sandwich system was mounted with silver paste onto this glass slide (Figure 1). By this way, the crystal was in thermal contact, but the electrodes were well isolated from the copper support. Electrical contact was made with thin lines of silver paste to the electrical circuitry that consisted of a high voltage supply and an electrometer. Glass windows in the thermostat vessel allowed for illumination of the dye covered crystal surface by a tungsten lamp through a monochromator. The photocurrents could be plotted by a recorder versus the exciting wavelength or versus temperature.

3. Experiments and Results

At room temperature, a current-voltage plot has been measured during illumination of the negatively biased dye covered crystal surface with light of 496 nm that corresponds to the maximum of the absorption band of the dye. It reveals the voltage range where the photocurrent leaves the steep increase of the space charge limited region [7] and is determined by the charge carrier injection process at the electrode. During photocurrent flow in this electrode limited region the crystal was cooled down by puring liquid nitrogen into the vessel. Thereby the photocurrent decreased by about two orders of magnitude when the temperature decreased down to 200 K. With the available light intensities the measurements of the present investigations were limited to this temperature range.

By current flow through the heating resistor a small heating rate of $q \approx 2 \text{ K min}^{-1}$ was achieved and the sensitized photocurrent was recorded versus temperature. It increased again by about two orders of magnitude for a temperature range of less than 100 K (Figure 2). Moreover, this increase occurred in steps with temperature intervals of about 15 K. The photocurrents reached the same value at room temperature as before cooling and were reversible for at least two runs. Afterwards damage of the probes could occur.

At room temperature, dark currents were usually more than one order of magnitude smaller than the photocurrents and their influence was negligible at

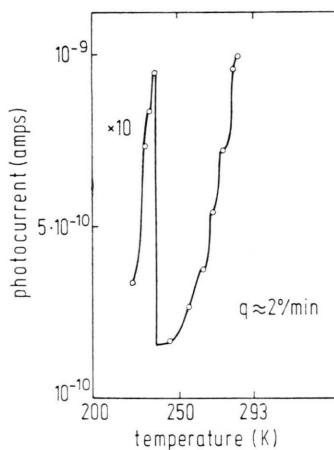


Fig. 2. Thermally stimulated sensitized photocurrent.

low temperatures. Cooling down during excitation of the sample and heating in the dark yields thermally stimulated photocurrents similar to those obtained with crystals between metal electrodes [8].

It is suggested that the overall process in course of the temperature dependent photocurrent can be described by an activation energy E_a according to

$$j = j_0 \exp \{-\Delta E_a/kT\}. \quad (2)$$

Indeed, plotting the points of Fig. 2 in a semi-logarithmic diagram $\log J$ vs. $1/T$ yields a straight line and an activation energy of $\Delta E_a = 0.26 \pm 0.02$ eV can be determined from the slope (Figure 3).

4. Discussion

The temperature dependence of the sensitized photocurrent can be discussed in terms of a reaction scheme. From Eq. (1) the rate for free carrier formation becomes in case of electron injection into p-chloranil

$$\frac{d[e_{CA}^-]}{dt} = k_{es}[D^+ \dots e_{CA}^-] - k_{re}[e_{CA}^-]. \quad (3)$$

The last term can be neglected under limiting current conditions ($[e_{CA}^-] \rightarrow 0$), and as to the first term the rate equation

$$\begin{aligned} \frac{d[D^+ \dots e_{CA}^-]}{dt} &= k_d[D^*] \\ &+ k_{re}[e_{CA}^-] - (k_{es} + k_r)[D^+ \dots e_{CA}^-] \end{aligned} \quad (4)$$

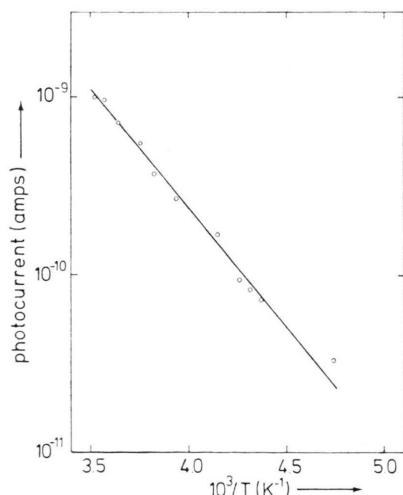


Fig. 3. Semilogarithmic plot of the sensitized photocurrent.

yields for steady state conditions

$$[D^+ \dots e_{CA}^-] = \frac{k_d}{k_r + k_{es}} [D^*] + \frac{k_{re}}{k_r + k_{es}} [e_{CA}^-]. \quad (5)$$

Neglecting again the last term, with Eq. (5) inserted into Eq. (3) the current density becomes

$$j = e k_d [D^*] k_{es} / (k_r + k_{es}) \quad (6)$$

and depends on the externally applied electric field as well as on the temperature via

$$k_{es} = k_{es,0} \exp \{-\Delta E_a/kT\}.$$

The excited cyanine dye has an energetic level with respect to an electron in vacuo at 3.4 eV [9], and p-chloranil is a strong electron acceptor with an electron affinity of 4.3 eV [10]. Therefore, the dissociation process with rate constant k_d should not depend on external parameters like temperature or an externally applied electrical field, and the activation energy of 0.26 eV has to be assigned to the charge separation process with rate constant k_{es} that governs at least at low temperatures the quantum efficiency for charge carrier escape from the coulomb well, $\Phi_{ES} = k_{es}/(k_{es} + k_r)$, and, thus, the photocurrent of Equation (6).

The coulomb well is given by the coulombic attraction of the electron within the crystal by its dye ion across the phase boundary (Fig. 4) and the superposition of an externally applied electrical field E :

$$\Phi(x) = -Ex - e/4\pi\epsilon\epsilon_0 x \quad (7)$$

with a maximum at

$$x_m = (e/4\pi\epsilon\epsilon_0 E)^{1/2}, \quad (8)$$

where ϵ is the dielectric constant of the crystal and ϵ_0 the vacuum permittivity. Inserting typical values for the example given in Fig. 2, i.e. $\epsilon = 3$, a thickness of the crystal of 50μ and an applied voltage of 200 V, yields $x_m = 109 \text{ \AA}$.

Because the excited state of the dye is higher than the conduction band in chloranil it can be assumed that the electron is injected with some excess energy into the crystal that is dissipated in subsequent collisions with the lattice [2a]. After thermalization an initial separation distance x_0 of the intermediate state ($D^+ \dots e_{CA}^-$) is reached within the coulomb well (Fig. 4) that corresponds to the maximum of a distribution of electrons — the center of gravity [11]. It should be related to the

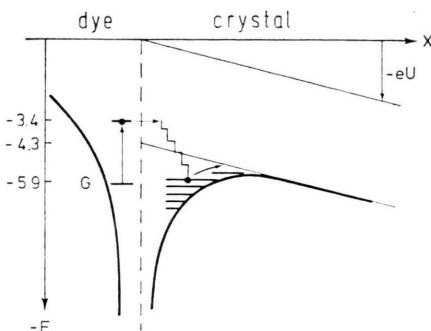


Fig. 4. Thermalization of an injected electron within the coulomb well and subsequent escape across the barrier from different lattice sites.

activation energy by the difference of the potential energy from the maximum

$$\Delta E_a = e[\Phi(x_m) - \Phi(x_0)]. \quad (9)$$

Inserting Eq. (7) with $x_m = 109 \text{ \AA}$ and $E = 4 \cdot 10^4 \text{ V cm}^{-1}$ yields $x_0 = 14 \text{ \AA}$. With the lattice parameter $c = 8.6 \text{ \AA}$ this corresponds approximately to the third molecular plane of the crystal. This is within the range of earlier results concerning thermalization distances in course of electron injection from tetrazene molecules into chloranil [2a].

The interesting features of the heating curves, the increase in steps (Fig. 2), suggests at first sight the excitation of vibrational modes of the dye as well as of the crystal. But the energy differences $\Delta E = k\Delta T$ are in the range of $\Delta E = 1.3 \cdot 10^{-3} \text{ eV} (\cong 10 \text{ cm}^{-1})$ and therefore too small by at least one order of magnitude. This amount corresponds rather to the difference of the potential energy of two neighbouring molecules in c -direction near the cusp of the potential well, indicating that the electrons in the crystal have their main distribution probability at lattice sites from where thermally stimulated release across the barrier is possible. With increasing distance from the maximum

towards the phase boundary, the molecules have an apparent increasing electron affinity due to the coulomb attraction by the dye ion. Therefore, with increasing temperature the diffusional motion of electrons starts from subsequently deeper lying sites until the initial separation distance x_0 is reached. This picture agrees with the experimental fact that the rate of released electrons increases with increasing temperature and reveals thus the density distribution within the coulomb well. Saturation should occur at higher temperatures, but more investigations are needed in this respect.

In the present treatment it has been assumed that the concentration of excited dye molecules remains constant in the whole temperature range [Equation (6)]. This is an oversimplification because cooling like adsorption closes non-radiative deactivation paths of the excited state [12]. Therefore, the decreasing photocurrent with decreasing temperature that is caused by injection kinetics may be cancelled to some extent by the increasing concentration of excited dye molecules. Measurements of the temperature dependent fluorescence intensity of a dye monolayer on a glass slide should give additional information concerning this point.

Finally, it has to be pointed out that the activation energy of 0.26 eV cannot be explained by the activation energy for the mobility of electrons in the conduction band of the crystal, that has been determined by time of flight measurements to be 0.1 eV within a limited temperature range of 40 K and is caused by smaller trapping of charge carriers [13]. But trapping should also influence the energetic and spacial distribution of electrons within the coulomb well.

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