Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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B. Nickel [a]

[a] Max-Planck-Institut für biophysikalische Chemie Abteilung, Spektroskopie, 34, Göttingen-Nikolausberg, Am Fassberg

Version of record first published: 28 Mar 2007.

To cite this article: B. Nickel (1972): Sensitized Photoconduction and Sensitized Delayed Fluorescence of Anthracene Single Crystals, Molecular Crystals and Liquid Crystals, 18:3-4, 227-261

To link to this article: http://dx.doi.org/10.1080/15421407208083596

Molecular Crystals and Liquid Crystals. 1972. Vol. 18, pp. 227–261

Sensitized Photoconduction and Sensitized Delayed Fluorescence of Anthracene Single Crystals

B. NICKEL

Max-Planck-Institut für biophysikalische Chemie
Abteilung Spektroskopie
34 Göttingen–Nikolausberg, Am Fassberg

Received January 28, 1972

Abstract—The literature on the sensitized photoconduction and the sensitized delayed fluorescence of anthracene single crystals is briefly reviewed. Some peculiarities of the heterogeneous system anthracene single crystal/aqueous dye solution are described which are important for the correct interpretation of experimental data.

The mechanism of sensitized hole injection, as proposed by Mulder and de Jonge, is confirmed for the dye rhodamine B: In the absence of strong oxidants and of heavy atoms and at high field strengths free holes are generated by CT-quenching of excited singlet states of the adsorbed dye, $^1D^*$, by the anthracene crystal, A. The quantum yield of the reaction $^1D^* + A \rightarrow D^{\dot{-}} + A^{\dot{+}}$ is ~ 1. Complications arising by the presence of strong oxidants are discussed in detail.

Triplet excitons are generated not only by triplet-triplet-ET, but also by recombination of the radical ions: $D^{\dot{-}} + A^{\dot{+}} \rightarrow D + {}^3A^*$. The often unusual time dependence of the sensitized delayed fluorescence of anthracene crystals is explained by an increase of surface quenching of triplet excitons during constant excitation.

With the same heterogeneous systems, but with reversed polarity, a weak sensitized delayed electron injection is observed. It is probably caused by the quenching of triplet excitons by semiquinone radicals $D^{\dot{-}}$.

1. Introduction

The photoconduction of molecular crystals$^{(1)}$ is often determined by the surface properties of the crystals. The best known example is the photoconduction of anthracene single crystals, which is caused in the near UV ($\lambda > 300$ nm) at high field strength by the quenching of excitons at the surface. However, apart from the fact that free charge carriers are generated at the surface, details about the processes occurring at the surface are usually not known. In this respect an anthracene single crystal with a suitable dye, e.g. rhodamine B, adsorbed on its surface is an exception. When either the adsorbed dye is excited in the visible or the anthracene in the near UV, the occurrence of the following processes can be demonstrated experimentally:

singlet-singlet-energy transfer (S-S-ET),
triplet-triplet-energy transfer (T-T-ET),
charge transfer quenching of excited singlet states (CT-Qu.),
formation of triplet states by recombination of radical ions,
triplet-triplet-annihilation (T-T-Annih.).

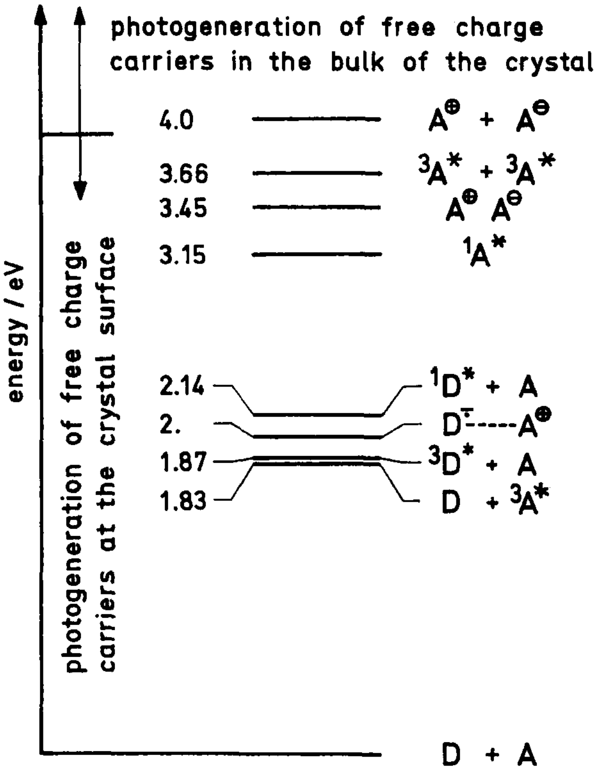

Figure 1. Energies of excited states of crystalline anthracene (A)(3) and of rhodamine B (D)(4). For completeness the energies of the postulated CT-exciton and of internal ionization of crystalline anthracene are included.(3) The energy of the ionpair $D^{\dot{-}} + A^{\oplus}$ follows from the results of the present paper.

The exceptional behaviour of this system has its origin in the relative energies of the excited states of the anthracene crystal *A* and the adsorbed dye *D* (Fig. 1). In principle one should observe the same reactions in homogeneous solution and some of them have been observed indeed.[5]

In order to explain the aim of the present paper it is necessary to briefly review published results and interpretations. In Fig. 2 the most important reactions are shown, which occur when either the dye or the anthracene single crystal are excited.

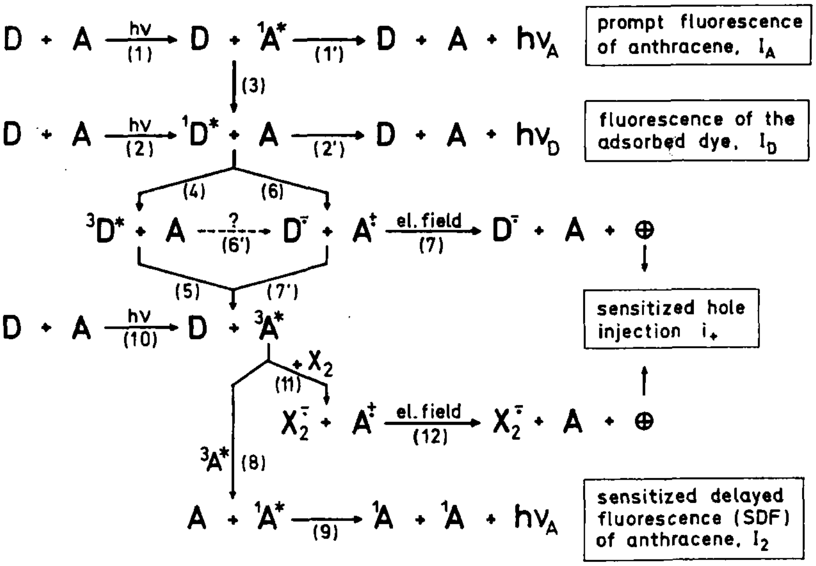

Figure 2. Reactions following the excitation of an anthracene single crystal *A* or of a dye *D*, adsorbed at the surface of *A*. X_2 is a strong oxidant. (1), (2), (10) correspond to excitation at $\lambda \leqq 420$ nm, $500 \text{ nm} < \lambda < 600$ nm, $\lambda = 633$ nm. Measurable quantities are shown in frames. Three important processes are omitted: Surface quenching of triplet excitons by other reactions than CT-Qu. (11), monomolecular decay of triplet excitons in the bulk of the crystal, and reoxidation of $D^{\bar{\cdot}}$ by a weak oxidant X_1.

Steketee and de Jonge[6] were the first to investigate the heterogeneous system. They used an electrolytic contact arrangement, developed by Kallmann and Pope[7] (Fig. 3). In sensitization experiments one of the aqueous electrolyte solutions was a dilute

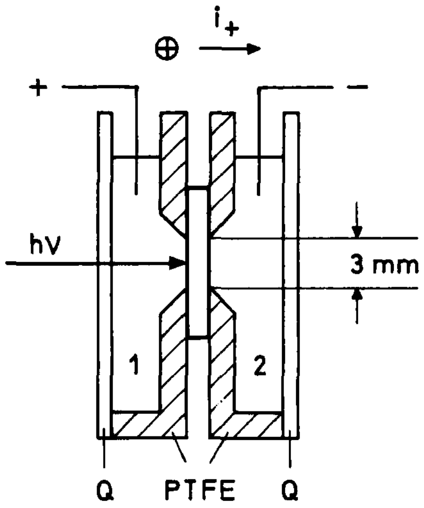

Figure 3. Sandwich arrangement for the measurement of the (photo-) conduction of anthracene single crystals *A*.⁽⁷⁾ The contacts 1 and 2 are aqueous electrolyte solutions; *Q* are quartz windows. In sensitization experiments solution 1 is a dilute solution of a dye.

solution of a dye. The dye was partly adsorbed on the surface of the crystal. Upon excitation with visible light (Fig. 2 (2)) a sensitized hole injection current i_+ (7) was found. The excitation spectrum of the photocurrent, $i_+(\tilde{\nu})$, was very similar to the absorption spectrum of the dye in homogeneous solution, $\epsilon(\tilde{\nu})$. Upon excitation with UV light, the photocurrent was increased by the adsorption of the dye, but the excitation spectrum $i_+(\tilde{\nu})$ was still parallel to the absorption spectrum of the anthracene crystal, $\alpha(\tilde{\nu})$ (parallel here means that maxima and minima of $i_+(\tilde{\nu})$ and $\alpha(\tilde{\nu})$ were at the same wavenumbers). The authors proposed that in both cases (vis and UV) the adsorbed dye was the primary electron acceptor, which is necessary for the surface generation of holes.

Mulder and de Jonge⁽⁸⁾ proposed a detailed reaction scheme for the sensitized generation of holes: An excited singlet state $^1D^*$ of the dye is produced either by direct excitation (2) or by primary excitation of the anthracene crystal (1) and subsequent S-S-ET (3). The electronically excited state of the dye molecule is quenched by CT interaction with anthracene—either directly via (6) or via (4), (6′).

In a later paper Mulder(9,10) demonstrated the S-S-ET (3) directly: In the near UV the excitation spectrum of the fluorescence of the adsorbed dye, $I_D(\tilde{\nu})$, was parallel to the absorption spectrum of the anthracene crystal $\alpha(\tilde{\nu})$. At the same time the fluorescence intensity of the anthracene crystal (1′) was decreased by the adsorption of the dye.

In a final paper(11) on sensitized photoconduction of anthracene Mulder determined the quantum yield η_{i_+} of sensitized hole injection by extrapolating i_+ to infinite voltage. For low concentrations of the adsorbed dye he obtained in some cases $\eta_{i_+} \sim 1$. So, if holes are indeed generated by the CT-Qu. (6), the quantum yield of this process, η_{CT}, must be ~ 1.

The phenomenon of sensitized photoconduction was independent of the relative triplet energies of the dye, $E(^3D^*)$, and of the anthracene crystal, $E(^3A^*)$. For $E(^3D^*) \geqq E(^3A^*)$ it was to be expected that triplet excitons $^3A^*$ are generated by energy transfer from the excited dye. Nickel, Staerk and Weller(12) demonstrated the sensitized generation of triplet excitons by the observation of the sensitized delayed fluorescence (SDF) of anthracene. They interpreted this result as T-T-ET (4), (5) and proposed an alternative mechanism for sensitized hole injection: CT-Qu. of triplet excitons with an oxidant X_2 (11).

Independently Michel-Beyerle and Willig(13) investigated the possible role of triplet excitons in sensitized hole injection. They generated triplet excitons in the bulk of the crystal by excitation with an He-Ne-laser (10) and measured the dependence of the photocurrent i_+ on the concentration of various oxidants X_2 and on the coverage of the crystal surface with dye. They could show that (11) is a possible mechanism of sensitized hole injection.

With reversed polarity (Fig. 3) in some cases a weak sensitized electron injection current i_- was found(12,14) and was attributed to CT-Qu. of triplet excitons by an (unknown) reductant R.

Nickel and Maxdorf(15) determined the diffusion constant $D_{c'}$ ($c' \perp a,b$-plane) of triplet excitons making use of the sensitized generation of triplet excitons. They obtained a very low value, which is however in satisfactory agreement with theoretical predictions and with the value obtained by Suna,(16) who used $D_{c'}$ as an adjustable parameter for the explanation of the magnetic field dependence of the delayed fluorescence of anthracene.

With the dye erythrosin a strong dichroism was observed in the absorption of light by the adsorbed dye, in sensitized hole injection i_+ and in sensitized generation of triplet excitons, k_0.(17) This was explained by an oriented adsorption of the dye. The excitation spectra $i_+(\tilde{\nu})$ and $k_0(\tilde{\nu})$ were found to be nearly identical for strongly absorbed light (polarization $\parallel$ a-axis); they were markedly different for weakly absorbed light (polarization $\parallel$ b-axis). This latter observation could only be explained by two assumptions: Not all adsorbed dye molecules are equivalent and the generation of triplet excitons and of free holes cannot proceed via (4), (5) alone.

SCOPE OF THE PRESENT PAPER

(1) The two proposed mechanisms of sensitized hole injection (Fig. 2 (6), (11)) do not necessarily exclude each other. However, it will be shown, that with no oxidant X_2 present and at high field strength free holes are predominantly generated by CT-Qu. of ${}^1D^*$ (6) and that the quantum yield η_{i_+} is high.

(2) It will be shown that triplet excitons are formed also by reaction (7): $D^{\overline{\cdot}} + A^{\overset{+}{\cdot}} \rightarrow D + {}^3A^*$.

(3) An explanation will be given for the often unusual time dependence of the SDF. It will be shown, that dye-dye interactions cannot be neglected.

(4) At high excitation intensities two-quantum processes become important for sensitized charge carrier injection. An example is sensitized electron injection.

Quantitative aspects of sensitized generation of triplet excitons will be treated in two subsequent papers.

2. Some Peculiarities of the System Anthracene Single Crystal plus Adsorbed Dye

An anthracene single crystal in contact with an aqueous dye solution is a rather complicated heterogeneous system. In order to interpret experimental results correctly one should have in mind some peculiarities of this system. Mulder(11) has carefully investigated the physical, chemical, and experimental factors which affect the sensitized photoconduction of anthracene. He limited his experiments to low excitation intensities, $I_0 < 10^{14}$ photons cm^{-2} sec^{-1}, and he measured the photocurrent with low time resolution. His work should be supplemented for two reasons. For the observation of a SDF it is normally necessary to use excitation intensities $I_0 > 10^{14}$ photons $\text{cm}^{-2}\,\text{sec}^{-1}$, because at low excitation intensities the intensity I_2 of SDF depends quadratically on the excitation intensity I_0: $I_2 \propto I_0{}^2$. With high excitation intensities, however, irreversible changes of the state of the system take place. Therefore the excitation must be limited to short times.

2.1. SENSITIZED DELAYED FLUORESCENCE—SDF

The SDF is much more sensitive to changes of the state of the system than the photocurrent. This is due to the fact that I_2 depends in the simplest case on four factors (see Fig. 4):

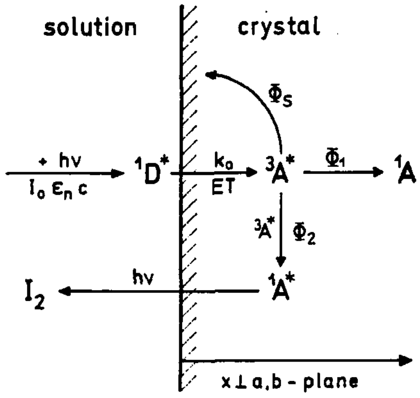

Figure 4. Connection between the excitation intensity I_0, the rate k_0 of sensitized generation of triplet excitons, the consumption of triplet excitons by surface quenching Φ_s, by monomolecular decay Φ_1, and bimolecular decay Φ_2, and the intensity I_2 of SDF of anthracene. The only assumption made with respect to the mechanism of the energy transfer ET is $k_0 \propto I_0$.

1. Generation of triplet excitons at the surface with the rate $k_0 \propto I_0$.
2. Surface quenching of triplet excitons with the rate $\Phi_s = k_s \cdot n(0)$. (k_s = surface quenching rate constant; $n(0)$ = concentration of triplet excitons at the surface.)

3. Monomolecular decay of triplet excitons in the bulk of the crystal with the rate

$$\Phi_1 = \beta \int_0^\infty n(x)\,\mathrm{d}x.$$

(β = monomolecular decay constant.)

4. T-T-annihilation in the bulk of the crystal with the rate

$$\Phi_2 = \gamma \int_0^\infty n(x)^2\,\mathrm{d}x.$$

(γ = T-T-annihilation rate constant.)

For low excitation intensities ($\Phi_1 \gg \Phi_2$) the relation $I_2 \propto \Phi_2$ holds for the intensity I_2 of SDF; for high intensities ($\Phi_1 \lesssim \Phi_2$) I_2 is only approximately proportional to Φ_2.(27) This case ($\Phi_1 \lesssim \Phi_2$) is the usual case for the experiments reported in this paper.

In the stationary state the following equations hold:

$$\begin{aligned} k_0 &= k_s n(0) + \beta \int_0^\infty n(x)\,\mathrm{d}x + \gamma \int_0^\infty n(x)^2\,\mathrm{d}x \\ &= \quad \Phi_s \quad + \quad \Phi_1 \quad + \quad \Phi_2 \end{aligned} \tag{13}$$

and for $x > 0$

$$D\frac{d^2n(x)}{\mathrm{d}x^2} - \beta n(x) - \gamma n(x)^2 = 0 \tag{14}$$

(D = diffusion constant of triplet excitons for the direction x). From Eqs. (13) and (14) the spatial distribution of triplet excitons, $n(x)$, and the intensity dependence of SDF, $I_2 = I_2(I_0)$ can be calculated.(27) Here it is sufficient to point out, that I_2 depends on k_0 and k_s. In most cases surface quenching is the dominating decay process for triplet excitons generated at the surface, i.e. $\Phi_s > \Phi_1 + \Phi_2$. This is the reason why I_2 is equally sensitive to changes of k_0 as to changes of k_s.

2.2. PROPERTIES OF THE SYSTEM ANTHRACENE SINGLE CRYSTAL/ ADSORBED DYE

The properties of this system are determined by the following factors:

(a) *The quality of the anthracene crystal*

It can be characterized partly by the lifetime $\tau = 1/\beta$ of triplet excitons in the bulk of the crystal.(18) The voltage dependence and the time dependence of measurable quantities are influenced by the presence of traps and by their concentration and energetic distribution.(1e)

(b) *Purity and structure of the surface*

The surface can be cleaned by rinsing the crystal with an organic solvent.(11) The quality of the surface can be judged by effects which depend markedly on the structure of the surface, as for example the dichroism found with erythrosin.(17)

(c) *Chemical factors*

The properties of the system depend on the composition of the aqueous solution in contact with the crystal: on the dye, the concentration of the dye, the pH, the ionic strength, the presence of oxygen, of redox systems, and of heavy atoms (e.g. iodide).(11)

(d) *Instability of the surface*

The surface of an anthracene crystal is not stable in contact with an aqueous solution. The surface is altered by dissolution and recrystallization of anthracene. In some cases the surface is stabilized by the adsorption of a dye, e.g. of erythrosin.(17) Which state of the surface is stabilized may therefore depend on the adsorption rate of the dye. With a 10^{-6} molar dye solution a maximum of the photocurrent i_+ or of the SDF I_2 is reached 2 to 10 min after the addition of the dye solution (the crystal is illuminated only for short times < 1 sec). The time during which reproducible values of i_+ and I_2 are measured depends strongly on the dye. It ranges from a few minutes (e.g. with pyronine (G) Y) to several hours (e.g. with erythrosin).

(e) *Different adsorption of dye molecules*

Not all adsorbed dye molecules are equivalent: i_+ is generally not proportional to the coverage of the surface with dye(11) and the excitation spectra $i_+(\tilde{\nu})$ and $k_0(\tilde{\nu})$ are generally not identical.(17) Possible reasons for this nonequivalence are:

1. A real surface of an anthracene single crystal is not a pure (001) plane. Different adsorption sites should therefore be distinguished in principle.
2. Even for an ideal surface the interaction of a dye molecule with the anthracene crystal may depend on the orientation of the dye molecule.

3. For a monolayer of adsorbed dye the average distance between neighbouring dye molecules is ~ 20 Å. Dye-dye interactions and especially formation of dye dimers therefore may be important.(11,17)

Hence, in the kinetic analysis of experimental data one should distinguish different classes of adsorbed dye molecules by using different sets of rate constants. In practice, however, one treats all adsorbed dye molecules as equivalent. For this reason one has to be very cautious in the interpretation of deviations from a kinetically expected behaviour.

2.3. Time Dependence of Measurable Quantities and its Consequences

The time dependence of the quantities i_+, i_-, I_2 is often other than expected. E.g. for the intensity I_2 of SDF according to Fig. 4 it is expected that I_2 increases monotonously and finally reaches a stationary value in a time comparable to the average lifetime $\bar{\tau}$ of triplet excitons in the bulk of the crystal. In contrast to this one often observes that I_2 reaches a maximum in a time $t_{\max} \ll \bar{\tau}$, and then decreases without reaching a true stationary state at all. If in such a case the dependence of I_2 on some external parameter is measured, e.g. the voltage dependence $I_2(V)$, the intensity dependence $I_2(I_0)$ or dependence of I_2 on the iodide concentration in the contact solution, one generally finds that the time dependence $I_2(t)$ changes too; examples are given in Fig. 8 and 10. If one plots in this case the maximum of I_2 or the value of I_2 at a definite time against the parameter under consideration, the significance of such a plot is quite uncertain, because the different points refer to different states of the system—not only with respect to the varied parameter. An adequate understanding of the time dependence therefore is essential for the correct interpretation of the parameter dependence.

In practice five types of time dependence can be distinguished:

(a) Prompt processes are defined as having a rise time $t_r < 1\,\mu s$. Examples are the prompt fluorescence (see Fig. 2): (1), (1′) and (2), (2′) and sensitized hole injection i_+ by (2), (6), if the transit time of free holes is $< 1\,\mu s$.

(b) Delayed processes which are determined by the lifetime of triplet states: $t_r \sim 10^{-5}$ to 10^{-2} sec. Examples: SDF, sensitized electron injection i_-.

(c) Reversible (chemical) changes of the state of the surface, e.g. partial reduction or oxidation of the adsorbed dye: $t_r \sim 10^{-3}$ to 1 sec. The initial state of the system is reached again after a dark period of about $10 t_r$ duration.

(d) Irreversible changes of the surface with long excitation times, t_{exc}: If an adsorbed dye molecule is excited ν times per second, "long excitation" means $t_{\text{exc}} \cdot \nu \gg 1$.

(e) Irreversible changes in the dark.

3. Experimental Section

3.1. SUBSTANCES

Anthracene (Fluka, puriss. for scintillation) was purified by vacuum sublimation and zone refining. The lifetime of triplet excitons in the purified anthracene was 14 ms. Thin anthracene single crystals were grown in solution.(19) A mixture of 98.5 vol. 1.2-dichloroethane and 1.5 vol. carbontetrachloride was used as solvent. 4.7 g anthracene were dissolved in 200 ml of the solvent mixture under nitrogen. With chromatographically purified solvents (basic Al_2O_3) the triplet lifetime of the solution grown crystals was 6 to 7 ms.

Dyes: Rhodamine B (Merck, p.a.) was used without purification. Eosin Y and erythrosin (both Merck) were purified chromatographically on neutral Al_2O_3 with water as solvent. The aqueous solutions of the purified dyes were used as stock solutions.

Solvents: doubly distilled water, acetonitrile (Merck, Uvasol).

Other chemicals: Merck, analytic reagent grade.

3.2. MEASURING CELL

The measuring cell is shown schematically in Fig. 5. A thin anthracene single crystal (area ~ 0.5 cm^2, thickness $\sim 30\ \mu$) was fixed with an epoxy resin to the flat end of a double-walled glass tube (inner ϕ 0.3 cm, outer ϕ 1.0 cm). The space between the two concentric tubes was filled with an electrolyte solution and electrically grounded. The inner tube was normally filled with an aqueous solution 10^{-2} M in Na_2SO_3 and in NaOH. The glass tube with the

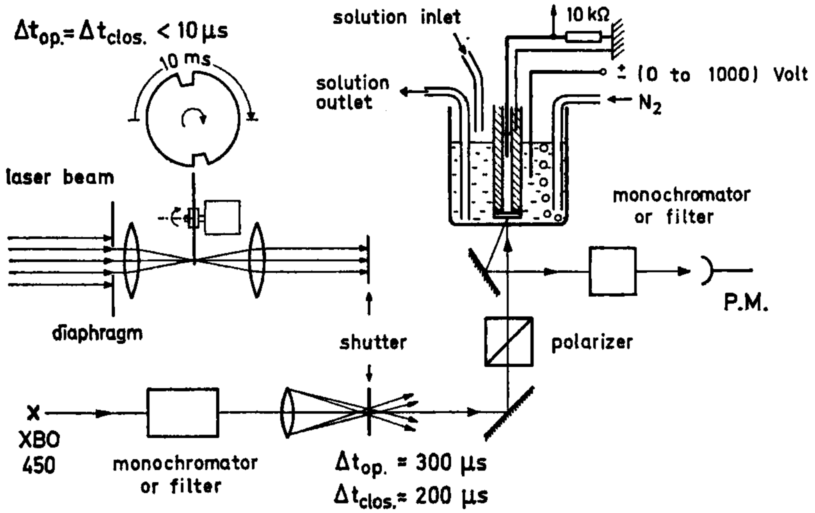

Figure 5. Experimental arrangement (schematically). Explanations are given in the text.

crystal dipped into a second aqueous electrolyte solution in a cylindrical quartz vessel. In sensitization experiments the outer solution was a dilute solution of a dye. A voltage was applied by two platinum wires. With this arrangement the dark current was 10^{-12} to 10^{-11} A at $2 \cdot 10^5$ V cm^{-1}.

3.3. PREPARATION OF THE SURFACE AND ADSORPTION OF THE DYE

Prior to the adsorption of the dye the crystal surface was rinsed(11) with a mixture of equal volumes of freshly distilled acetone and doubly distilled water. With rhodamine B and eosin Y the intensity I_2 of SDF was found to be 2 to 3 times higher when the freshly rinsed crystal was dipped first into a dye-free and oxygen-free reducing electrolyte solution, e.g. 0.1 M Na_2SO_3, which was replaced 5 to 10 minutes later by a solution containing the dye. Adsorbed oxygen is consumed by the reducing agent. However, it is not clear whether consumption of adsorbed oxygen is the correct explanation, since with erythrosin the highest values of I_2 were found when the freshly rinsed crystal was dipped immediately into the dye solution. The properties of the surface depend on the solvent used for cleaning the surface.(17) This requires further investigation.

Oxygen was excluded by bubbling purified presaturated nitrogen through the measuring cell and through the solutions before they were introduced into the cell.

The distance between the crystal surface and the quartz window of the cell was < 1 mm. Therefore absorption of light by the dye solution could be neglected up to 10^{-5} M dye solutions.

The measuring cell was thermostated in all experiments to 22 °C.

3.4. Excitation

(a) Polychromatic excitation with a xenon arc lamp XBO 450/1 (Osram), combined with a heat absorption filter and a cut-off filter OG 515 (3 mm) (Schott).

(b) Excitation with an argon-ion laser 52 A (Coherent Radiation Laboratories) at 514.5 nm. Disturbing components of the plasma light were removed with a dispersion prism and diaphragms. The light intensity was measured with a Model 212 power meter (Coh. Rad. Lab.).

The diameter of the laser beam falling onto the crystal was limited to 2 mm or 3 mm by diaphragms. In order to estimate the homogeneity of illumination it was assumed that the radial intensity distribution $I_0(r)$ is gaussian: $I_0(r) \propto \exp(-r^2/\rho^2)$ with $\rho = \text{const.}$ From the ratio of the intensities measured with the two diaphragms it was calculated $I_0(1.5\text{ mm}) \approx 0.8\, I_0(0)$. Thus the illumination was homogeneous within $\pm 10\%$.

3.5. Shutter

When the xenon lamp was used the light was focused on the central part of a Compur camera shutter (2–3 mm diameter). The time required for full opening, $\Delta t_{\text{op.}}$, and full closing, $\Delta t_{\text{clos.}}$, of the shutter was 300 μs, resp. 200 μs. The shortest exposure time was 4 ms.

With the laser beam a fast mechanical shutter was realized by combining a chopper with a shutter (Fig. 5). The laser beam was focused and made parallel again by two lenses. The focus was in the plane of the chopper (3000 rpm, 14 cm diameter). The exposure time was given by the opening angle of the chopper. The chopper consisted of two blades; thus the opening angle could be varied continuously. Limitation to one single illumination was achieved with the additional shutter. It was found $\Delta t_{\mathrm{op.}} = \Delta t_{\mathrm{clos.}} < 10\ \mu\mathrm{s}$. Two or more exposures with a dark period of ~ 10 ms between exposures were used to find out whether fast reversible changes of the system had occurred during illumination.

3.6. Fluorescence Measurements

Two different emissions could be measured simultaneously (in Fig. 5 the second emission is measured in the direction perpendicular to the plane of the figure with a second mirror). The SDF was normally measured with a Schott blue filter BG 12 (8 mm) and a RCA 1 P 21 photomultiplier. The fluorescence of the dye was measured with a cut-off filter, which absorbed the stray excitation light, and with a 1 P 21 photomultiplier. The fluorescence of the filter was negligible. However, the fluorescence of the epoxy resin, used for the fixation of the crystal, could not be neglected and care was taken to avoid direct excitation of the resin.

The lifetime $\tau_{\mathrm{T}} = 1/\beta$ of triplet excitons in the bulk of a crystal was determined from the lifetime τ_{DF} of nonsensitized DF: $\tau_{\mathrm{T}} = 2\tau_{\mathrm{DF}}$.(2) The crystal was homogeneously excited with orange-red light.

3.7. Electronic Equipment

A Tektronix Type 565 dual-beam oscilloscope with a differential amplifier 2 A 63 and a dual trace amplifier 3 A 72 was used. In some cases the Keithley amplifiers 610 B and 417 were used as preamplifiers.

The lifetime τ of triplet excitons was in some cases determined with a PAR Waveform Eductor model TDH-9.

3.8. Thickness of the Crystals

The thickness of the crystals was measured with a Carl-Zeiss Lichtschnitt-Microscope. The microscope was calibrated with a crystal whose average thickness was known from its area and its weight.

3.9. Fluorescence Quenching Experiments

The experimental proof of the quenching of the fluorescence of rhodamine B by anthracene in homogeneous solution was expected to be difficult because of the low solubility of anthracene in polar solvents. For this reason the first experiments were made at higher temperature than room temperature. It turned out, however, that anthracene solutions in acetonitrile are quite easily supersaturated, and that the supersaturated solutions are sufficiently stable when cooled down to room temperature (5 to 10 minutes).

Glass tubes (Duran 50) were used as fluorescence cuvettes. Each tube contained a small glass-sealed magnetic stirrer, a known quantity of solid anthracene and 4 ml of a $5 \cdot 10^{-6}$ M solution of rhodamine B in acetonitrile, which was additionally $5 \cdot 10^{-5}$ M in HCl in order to compensate the alkaline reaction of the glass. The solutions were degassed and sealed. The increase of volume by solid anthracene was taken into account as a correction.

For the fluorescence measurements a thermostated tightly fitting brass tube was used with two bores for excitation and fluorescence. The rhodamine B was excited approximately at 540 nm; the fluorescence was measured with an orange filter OG 575 (2 mm) (Schott) and a RCA 1 P 21 photomultiplier.

The solid anthracene was dissolved by heating to 60 to 80 °C. The solutions were cooled down in the thermostated brass tube. The fluorescence intensity F increased with decreasing temperature. After five minutes a value of F was reached, that remained constant for 5 to 10 minutes up to the beginning of the crystallization of anthracene.

4. Mechanism of Sensitized Hole Injection†

Two different mechanisms of sensitized hole injection have been proposed (see Fig. 2 (6) and (4), (5), (11)). If free holes are generated predominantly by the direct CT-reaction

$$^1D^* + A \rightarrow D^{\overline{\cdot}} + A^{\dot{+}}, \tag{6}$$

it should be possible to verify (6) experimentally. The consequences of (6) are:

(a) The sensitized injection of holes is a prompt process (see Sec. 2.3).

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† Reported at the Second International Symposium on Organic Solid-State Chemistry, in Rehovot, Israel, Sept. 14–18, 1970.

(b) The fluorescence of the adsorbed dye is quenched by the anthracene crystal.

(c) The dye D is the primary electron acceptor, i.e. there is no need for an additional electron acceptor X_2 as in reaction (11).

(d) The adsorbed dye D is reduced to $D^{\overline{\cdot}}$ by the CT-Qu. of $^1D^*$. If the recombination of the radical ions $D^{\overline{\cdot}}$ and $A^{\dot{+}}$ is prevented by an applied voltage and if a fast reoxidation of $D^{\overline{\cdot}}$ by some oxidant X_1 is excluded, the concentration of D and therefore the photocurrent i_+ should decrease during constant illumination.

(e) Intersystem crossing (4) competes with CT-Qu. (6). Increase of the intersystem crossing (ISC) rate by the addition of iodide should give a decrease of the photocurrent i_+.

The deductions (a) to (e) were verified experimentally with the dye rhodamine B.

To (c) and (d)

A change of the concentration c of the adsorbed dye can be measured by the change of the fluorescence intensity I_D of the adsorbed dye at constant illumination. However, the dye being adsorbed from an aqueous dye solution, one encounters the experimental difficulty that, in addition to adsorbed dye, dissolved dye is also present, and that the quantum yield of the fluorescence of the adsorbed dye is much lower than that of the dissolved dye. This difficulty was partly overcome by using a very dilute solution of rhodamine B (10^{-8} M), by replacing this solution by a dye-free electrolyte solution, after sufficient dye had been adsorbed, and by keeping the distance between crystal surface and quartz window as small as possible. With this procedure applied, a substantial fraction of the observed dye fluorescence originated from the adsorbed dye.

Figure 6 gives the result of an experiment, in which oxidants had been excluded as far as possible:

1. No voltage applied. The fluorescence intensity I_D of the dye remained constant during illumination.
2. +800 volt applied. The photocurrent i_+ and the fluorescence intensity I_D decreased during illumination. The two "stationary" values $i_{+\text{stat}}$ and $I_{D\text{stat}}$—the dashed lines in Fig. 6—were chosen in order to represent the time dependence of $i_+(t) - i_{+\text{stat}}$ and $I_D(t) - I_{D\text{stat}}$ by exponential functions.

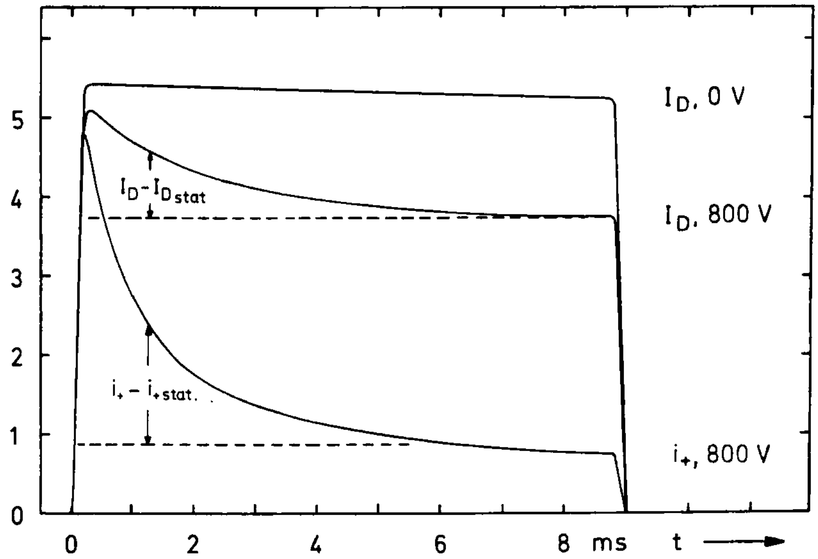

Figure 6. Time dependence of the fluorescence I_D of adsorbed and dissolved rhodamine B ($< 10^{-8}$ M) at 0 volt and +800 volt, and of the hole injection current i_+ at +800 volt. Crystal thickness 17μ ($\triangleq 5 \cdot 10^5$ V cm^{-1}); triplet lifetime $\tau \approx 1$ ms; electrolyte 0.02 M NaCl; excitation intensity $I_0 \approx 1.0 \cdot 10^{19}$ photons cm^{-2} sec^{-1}, $\lambda = 514$ nm. The rise time of I_D and i_+ is determined by the shutter.

In both cases the electrolyte was NaCl. In a following experiment NaCl was replaced by $2 \cdot 10^{-2}$ M $NaHSO_3$. $NaHSO_3$ is a sufficiently strong oxidant† for the oxidation of the semiquinone radical $D^{\cdot}$. It was found, that with $NaHSO_3$ present I_D remained constant even with +800 volt applied and i_+ decreased only by 10% during illumination.

In these experiments also the SDF I_2 was measured. With NaCl and +800 V a fast decrease of I_2 was found. With 0.02 M $NaHSO_3$

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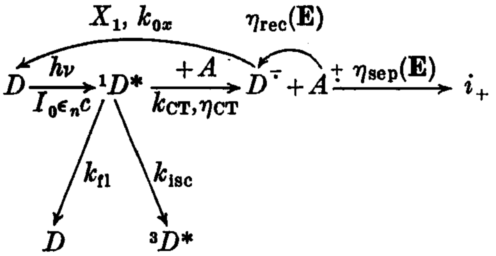
† The standard potential of the reversible reaction $S_2O_4^{--} + 2H_2O \rightleftarrows 2H^+ + 2HSO_3^- + 2\ominus$ is -0.01 volt[20]; at pH 6 the redoxpotential is -0.18 volt. The polarographically determined reduction potential of rhodamine B at pH 7 is -0.54 volt vs. normal hydrogen-electrode.[21] Principally one cannot exclude CT-Qu. of triplet excitons by HSO_3^-. However, the intensity of the SDF was found to be independent of the concentration of $NaHSO_3$. Perhaps HSO_3^- ions are not adsorbed or the CT is a slow reaction as compared with other quenching reactions of triplet excitons.

I_2 remained constant during the illumination; but with increasing voltage I_2 decreased strongly.

From the time dependences $i_+(t)$ and $I_D(t)$ in Fig. 6 it is possible to evaluate the quantum yield of hole injection, η_{i_+}. The evaluation is based on the following reaction scheme:



(15)

The adsorbed dye is excited with the rate $I_0\epsilon_n c$ (ϵ_n = natural molar absorption coefficient of the dye; c = surface concentration of the dye). The quantum yields of the competing processes, charge carrier recombination and separation, $\eta_{rec.}$ and $\eta_{sep.}$, are determined by the electric field $\mathbf{E}$:

$$\eta_{sep.} = \eta_{sep.}(\mathbf{E})\,; \quad \eta_{sep.} + \eta_{rec.} = 1 \tag{16}$$

When $D^{\dot{-}}$ is not reoxidized by surface recombination of holes, it is slowly reoxidized by some (unknown) oxidant X_1. It is assumed that the reaction $D^{\dot{-}} + A^{\dot{+}} \rightarrow D + A$ (or ${}^3A^*$) is much faster than the reaction $D^{\dot{-}} + X_1 \rightarrow D + X_1{}^{\dot{-}}$.

Assuming that the concentrations $[{}^1D^*]$ and $[{}^3D^*]$ can be neglected in comparison to $[D] + [D^{\dot{-}}] = c_0$, and with $\mathrm{d}[{}^1D^*]/\mathrm{d}t = \mathrm{d}[{}^3D^*]/\mathrm{d}t = 0$ one obtains

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -I_0 \cdot \epsilon_n \cdot \eta_{CT} \cdot \eta_{sep} \cdot c + k_{ox}(c_0 - c) \tag{17}$$

With $c = c_{stat}$ in the stationary state k_{ox} can be eliminated:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\mathrm{d}(c - c_{stat})}{\mathrm{d}t} = -I_0\epsilon_n\eta_{CT}\eta_{sep}\frac{c_0}{c_0 - c_{stat}}(c - c_{stat}) \tag{18}$$

and

$$\frac{\mathrm{d}\ln(c - c_{stat})}{\mathrm{d}t} = -I_0\epsilon_n\eta_{CT}\eta_{sep}\frac{c_0}{c_0 - c_{stat}} = -B \tag{19}$$

$(I_D(t) - I_{Dstat})$ and $(i_+(t) - i_{+stat})$ in Figs. 6 should be proportional to

$(c(t) - c_{\text{stat}})$. It was found $B(I_D) = 4.6 \cdot 10^2\ \text{sec}^{-1}$ and $B(i_+) = 6.3 \cdot 10^2\ \text{sec}^{-1}$. The two values of B agree reasonably well.

From (19) the quantum yield of hole injection, η_{i_+}, can be determined:

$$\eta_{i_+} = \eta_{\text{CT}} \cdot \eta_{\text{sep}} = \frac{B}{\epsilon_n \cdot I_0} \frac{c_0 - c_{\text{stat}}}{c_0} \tag{20}$$

With $B = 5 \cdot 10^2\ \text{sec}^{-1}$, $\epsilon_n = 2.3 \cdot 3 \cdot 10^7\ \text{cm}^2\ \text{mol}^{-1}$ at 514 nm, $I_0 = 1.6 \cdot 10^{-5}$ Einstein $\text{cm}^{-2}\ \text{sec}^{-1}$ and $(c_0 - c_{\text{stat}})/c_0 = 0.83$,

$$\eta_{i_+} \approx 0.4 \tag{21}$$

is obtained. The photocurrent i_+ at $+800$ V was not yet the limiting current $i_{+\infty}$, i.e. $\eta_{\text{sep}} < 1$, and therefore $\eta_{\text{CT}} > 0.4$. This value is in good agreement with Mulder's result⁽¹¹⁾

$$\lim_{V \to \infty} \eta_{i_+} \sim 1,$$

obtained under comparable experimental conditions.

From the photocurrent density at $t = 0$, $i_+(0) = 1.0 \cdot 10^{-4}\ \text{A cm}^{-2}$ (illuminated area $\approx 0.03\ \text{cm}^2$) the concentration c_0 was calculated:

$$c_0 = i_+(0)/I_0 \cdot \epsilon_n \cdot \eta_{i_+} \cdot N_L \cdot e = 2.4 \cdot 10^{-12}\ \text{mol cm}^{-2} \tag{22}$$

(e = elementary charge). This corresponds to 7000 Å²/adsorbed dye molecule or to a coverage of the surface with dye of approximately 2%.⁽¹¹⁾

The main uncertainty in the above calculation is the value of ϵ_n because the orientation of the adsorbed dye molecules cannot be expected to be completely isotropic. Nevertheless the order of magnitude of the result (21) should be correct.

To (b)

It was found qualitatively that the quantum yield $\eta_{\text{fl.}}$ of the fluorescence of the adsorbed dye was much lower than that of the dissolved dye.

The CT-Qu. of $^1D^*$ should also occur in homogeneous solution. For this reason the quenching of the fluorescence F of rhodamine B in acetonitrile by anthracene was investigated. The results are shown in Fig. 7. The fluorescence of rhodamine B is efficiently quenched by anthracene. $F_0/F = 2.0$ at 0.06 M anthracene indicates that the quenching cannot be much slower than diffusion controlled.

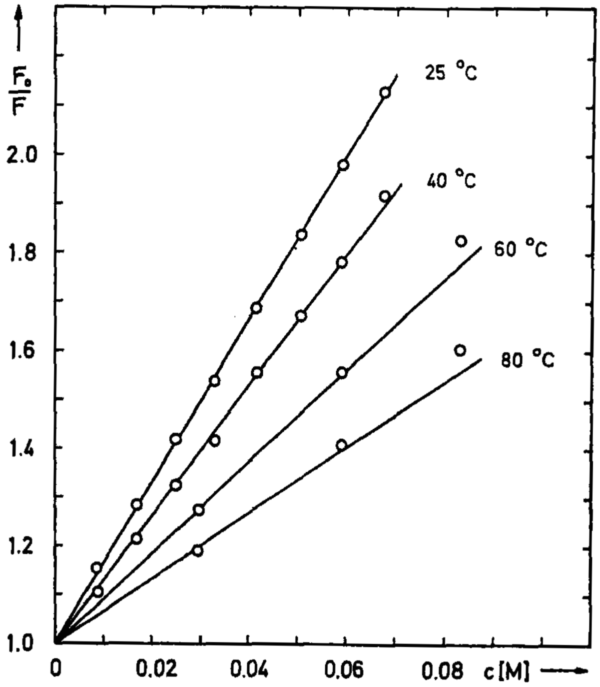


Figure 7. Quenching of the fluorescence F of rhodamine B by anthracene in acetonitrile. c = concentration of anthracene; F_0/F = reciprocal relative fluorescence intensity.

The decreasing quenching efficiency of anthracene with increasing temperature is caused by the strong decrease of F_0 itself, i.e. of the lifetime of $^1D^*$. It was found:

$$F_0(80\,°\mathrm{C}) \approx 0.25 F_0(25\,°\mathrm{C}).$$

This investigation should be complemented by flash experiments in order to prove that the quenching is caused by charge transfer (6), i.e. one should detect the radical ions $D^{\overline{\cdot}}$ and $A^{\dot{+}}$.

To (e)

In Fig. 8 the influence of iodide on the intensity I_2 of SDF and on the photocurrent i_+ is shown. The applied voltage was deliberately chosen to be small in order that $i_+ \ll i_{+\infty}$. The reason for this will become clear in Sec. 5. Two observations are made:

1. i_+ is decreased and I_2 is increased by the addition of iodide.
2. The time dependences $i_+(t)$ and $I_2(t)$ are altered by the addition of iodide. This will be discussed in Sec. 6.

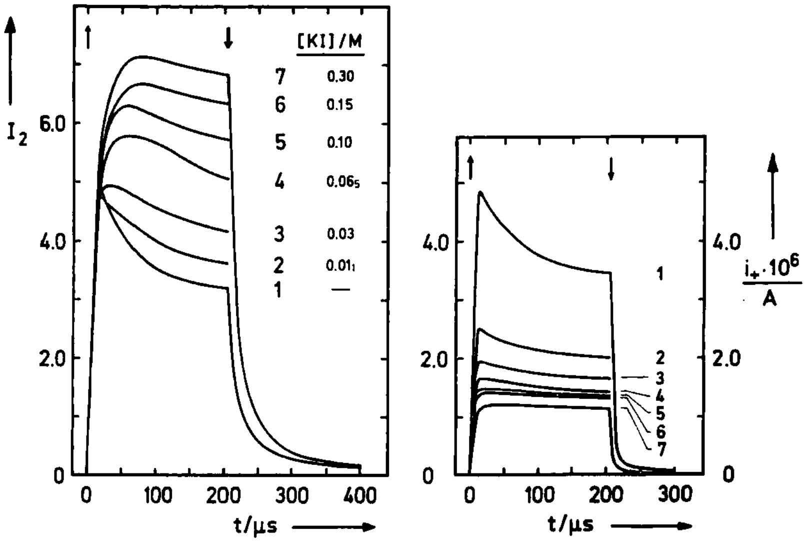


Figure 8. Influence of iodide on the SDF I_2 and the photocurrent i_+. $5 \cdot 10^{-7}$ M rhodamine B, $4.5 \cdot 10^{-2}$ M $NaHSO_3$, $5 \cdot 10^{-3}$ M Na_2SO_3 (pH $\approx$ 6); the ionic strength was kept constant by Na_2SO_4 to $J \approx 1$ (SO_4^{--} does not quench the fluorescence of rhodamine B). Triplet lifetime $\tau \approx 7$ ms; crystal thickness 34 μ; illuminated area 0.07 cm^2; voltage +300 V; $I_0 \approx 1.0 \cdot 10^{19}$ photons cm^{-2} s^{-1}, $\lambda = 514$ nm.

Despite the observation 2 it is obvious, that in the "stationary" state (see Sec. 2.3) an increase in the concentration $n(0)$ of triplet excitons at the surface is accompanied by a decrease in the photocurrent. This clearly contradicts a dominating generation of free holes by surface quenching of triplet excitons (see Fig. 2 (11)).

To (a)

The hole injection i_+ was always found to be a prompt process. Figure 9 gives an example. The experimental conditions were the same as in Fig. 8, curves 7; only the excitation intensity I_0 was lower by a factor 3.

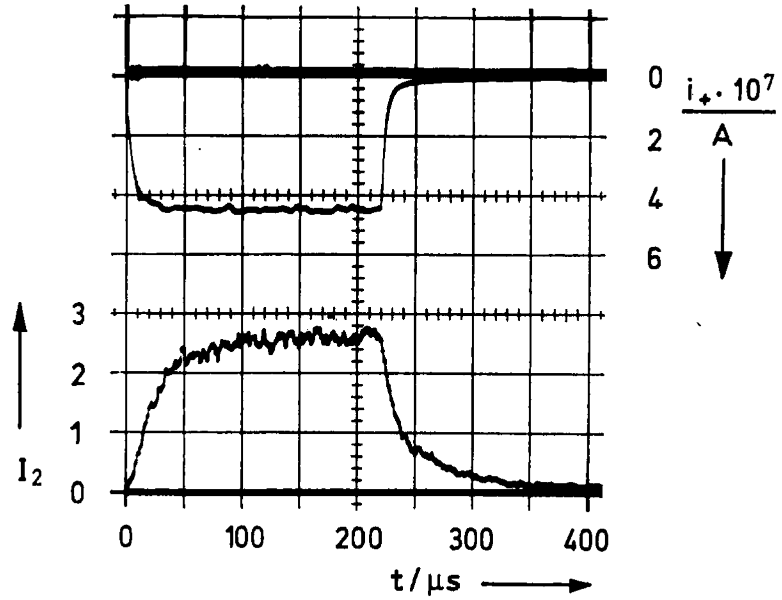


Figure 9. " Prompt " hole injection i_+ and sensitized delayed fluorescence I_2 of anthracene. The experimental conditions are the same as in Fig. 8, curves 7. The excitation intensity was lower by a factor 0.34: $I_0 \approx 3.4 \cdot 10^{18}$ photons cm^{-2} s^{-1}, $\lambda = 514$ nm. The time base was triggered by i_+.

Figure 9 shows that the photocurrent is essentially a prompt process. A small delayed component of i_+ is to be seen, however. This is probably caused by the surface quenching of singlet excitons (Fig. 2 (3)): At high excitation intensities T-T-annihilation is one of the dominating decay processes for triplet excitons (referring to Eq. (13), this means $\Phi_2 \sim \Phi_s + \Phi_1$). A substantial fraction of the singlet excitons is quenched at the surface by S-S-ET.

Conclusion: When no *strong* oxidant is present, free holes are generated predominantly by the direct CT-Qu. of ${}^1D^*$. The complications arising from the presence of strong oxidants are discussed in Sec. 8.3.

5. Mechanisms of Sensitized Generation of Triplet Excitons

5.1. Triplet-triplet-energy Transfer (T-T-ET).

T-T-ET has been proposed to be the mechanism of sensitized generation of triplet excitons.(12) The main arguments in favour of this mechanism are:

(a) In homogeneous solution the corresponding T-T-ET is well known.(5)

(b) The highest intensities I_2 of SDF were found with erythrosin, i.e. with a dye with a high intersystem crossing rate constant k_{ISC}.

(c) Increase of the intersystem crossing rate with iodide in the case of rhodamine B gave an increase of I_2 which may be due to an actual increase of the generation rate k_0 of triplet excitons (but see Sec. 6.4).

However, assuming that the primary processes of CT-Qu.

$$^1D^* + A \rightarrow D^{\cdot -} + A^{\cdot +} \qquad (6)$$

and of ISC and T-T-ET

$$^1D^* + A \rightarrow {}^3D^* + A \rightarrow D + {}^3A^* \qquad (4),(5)$$

do not depend on the electric field, and that the concentration of the adsorbed dye D is essentially constant even if a voltage is applied, one should expect that the SDF does not depend on the electric field. In contrast to this expectation it was found that I_2 decreases with increasing photocurrent i_+ (Fig. 10). The influence of the applied field on the time dependence $I_2(t)$ of the SDF is discussed in Sec. 6.3.

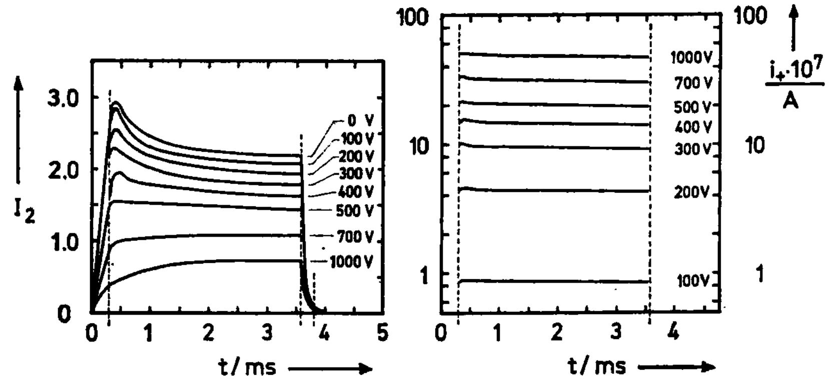


Figure 10. Voltage dependence of the SDF I_2 and hole injection current i_+. The vertical dashed lines mark the full opening of the shutter. 10^{-6} M rhodamine B, 0.09 M $NaHSO_3$, 0.01 M Na_2SO_3, 0.5 M KCl, pH ≈ 6. Excitation with XBO 450, filter OG 530 (3 mm) and interference band filter λ_{max} = 556 nm. Triplet lifetime ≈ 1 ms.

At low dye concentrations the voltage dependence of I_2 is still more pronounced and the time dependence $I_2(t)$ is nearly independent of the voltage.(22)

The simplest explanation of the voltage dependence of I_2 is the assumption that triplet excitons are generated by the recombination (7′): $D^{\dot{-}}+A^{\dot{+}} \rightarrow D+{}^3A^*$. Thus, the generation of triplet excitons and the final injection of holes (7), measured by i_+, are at least partially competing processes:

$$\begin{tikzcd} & D^{\dot{-}}+A+\oplus \\ D^{\dot{-}}+A^{\dot{+}} \arrow[ur, "\text{el. field}", "(7)"'] \arrow[dr, "(7')"'] & \\ & D+{}^3A^* \end{tikzcd} \qquad (23)$$

5.2. RECOMBINATION OF $D^{\dot{-}}$ AND $A^{\dot{+}}$

Besides the observed field dependence of the SDF the following arguments can be advanced for the generation of triplet excitons by the recombination (7′):

(a) In homogeneous solution the formation of triplet states by CT-Qu. of excited singlet states and subsequent recombination of the radical ions is now known to be a quite general phenomenon. This has been shown in a series of papers by Weller and coworkers.(23)

(b) The energetic requirements for the formation of triplet excitons by reactions (6) and (7′) are illustrated in Fig. 1. The occurrence of reaction (6) has been proved for rhodamine B in Sec. 4. Thus one can assume

$$E({}^1D^*+A) \gtrsim E(D^{\dot{-}}+A^{\dot{+}}).$$

The energetic requirement for reaction (7′),

$$E(D^{\dot{-}}+A^{\dot{+}}) \gtrsim E(D+{}^3A^*),$$

is fulfilled, for otherwise triplet excitons should be quenched by charge transfer and no SDF should be found.

(c) The voltage dependence $I_2(V)$ of the SDF is low if the intersystem crossing rate is high. For a given crystal the decrease of I_2 by an applied voltage is much lower with erythrosin than with rhodamine B.(22)

(d) The voltage dependence $I_2(V)$, measured with rhodamine B, is decreased by the addition of iodide—compare Sec. 4(e) and Fig. 8.

With a 0.1 M iodide solution as contact I_2 was practically independent of the voltage up to $3 \cdot 10^5$ V cm^{-1}.(22)

5.3. CONCLUDING REMARK

The generation of triplet excitons by the two different mechanisms will be investigated quantitatively in a later publication. For the present purpose it is sufficient to emphasize that normally both mechanisms have to be taken into account, and that with rhodamine B in absence of heavy atoms the CT-recombination-mechanism seems to be the dominating one.(22)

6. Time Dependence $I_2(t)$ of the SDF

In Sec. 2.3 it was stated that the experimentally found time dependence $I_2(t)$ is often quite different from that expected on the basis of the model in Fig. 4. Examples are given in Figs. 8 and 10. In Sec. 2.1 it was shown that I_2 depends on four quantities: the generation rate of triplet excitons, k_0, the surface quenching rate constant k_s, the monomolecular decay constant β, and the T-T-annihilation rate constant γ. A decrease of I_2 during constant illumination can be explained by a change of one or several of the "constants" k_0, k_s, β, γ. A decrease of γ is very improbable. Therefore the discussion is limited to possible changes of k_0, k_s, and β.

6.1. TIME DEPENDENCE OF k_0

The maximum decrease of k_0, $(\mathrm{d}k_0/\mathrm{d}t)_{\max}$, is given, if the adsorbed dye is reduced with the quantum yield 1 by the reactions (2), (6), (7) in Fig. 2. With this maximum rate of dye consumption about 50% of the initial decrease of I_2 (1) and i_+ (1) in Fig. 8 can be explained. But the experimental conditions were in fact such that the surface recombination (7′) of $D^{\overline{\cdot}}$ and $A^{\overset{+}{\cdot}}$ was the dominating process, following CT-Qu. (6), and, additionally, $NaHSO_3$ was present, in order to ensure the reoxidation of $D^{\overline{\cdot}}$. Thus a decrease of k_0 is ruled out as an explanation of the observed time dependence of I_2 in Fig. 8. The same is true for $I_2(t)$ in Fig. 10.

6.2. TIME DEPENDENCE OF β

β can increase during illumination if hole traps are filled and if triplet excitons are quenched by trapped holes. The probability of trap filling decreases with increasing applied voltage. The time dependence $I_2(t)$ in Fig. 10 may be partly due to this effect, because the purity of the anthracene crystal was low as seen by the short lifetime of the triplet excitons.

The time dependence $I_2(t)$ in Fig. 8 is probably not caused by an increase of β because of the higher quality of the anthracene crystal and of the fact that the addition of iodide to the contact solution was sufficient to give a normal time dependence of I_2.

6.3. TIME DEPENDENCE OF k_s.

The surface quenching constant k_s can increase during the illumination if a quencher for triplet excitons is formed. A possible quencher is the semioxidized dye, $D^{\dot{+}}$. According to Lindqvist⁽²⁴⁾ the semioxidized dye, $D^{\dot{+}}$, and the semireduced dye, $D^{\dot{-}}$ are formed in the reaction

$$^3D^* + D \rightarrow D^{\dot{+}} + D^{\dot{-}} \tag{24}$$

The occurrence of reaction (24) at the surface of an anthracene crystal is favoured by the following factors:

(a) High dye concentration.

(b) $E(^3D^*) \approx E(^3A^*)$, i.e. reaction (24) can compete with the T-T-ET.

(c) Besides strongly adsorbed dye molecules D_{ad} weakly adsorbed or dissolved dye molecules D are present, for which the interaction $D^* \ldots D$ or $D^* \ldots D_{\mathrm{ad}}$ is more important than the interaction $D^* \ldots A$ ($D^* = {}^1D^*$ or ${}^3D^*$).

(d) Long lifetime of $^3D^*$, τ_3.

With very low concentrations of rhodamine B (10^{-8} M) a normal time dependence of I_2 was found.⁽²²⁾ This confirms (a). With erythrosin ($\tau_3 \sim 10^{-4}$ s) an approximately normal time dependence of I_2 was found, with eosin Y ($\tau_3 \sim 10^{-3}$ s) a pronounced maximum of $I_2(t)$ was found. This different behaviour may be caused mainly by the difference of τ_3.

If triplet excitons are quenched by the reaction

$$D_{\mathrm{ad}}^{\dot{+}} + {}^3A^* \rightarrow D_{\mathrm{ad}} + A^{\dot{+}} \tag{25}$$

and if the injected holes are drawn into the crystal, then the quencher

$D_{ad}^{\dot{+}}$ is consumed by the CT-Qu. (25) of triplet excitons. If reaction (25) is followed by the reaction

$$D_{ad} + A^{\dot{+}} \rightarrow D_{ad}^{\dot{+}} + A, \tag{26}$$

the quencher is regenerated. Therefore, with increasing field strength the average number of triplet excitons quenched by one $D_{ad}^{\dot{+}}$ decreases. In this way the voltage dependence of $I_2(t)$ in Fig. 10 may be explained: With increasing voltage the generation rate of triplet excitons decreases because of reaction (23), but at the same time the increase of k_s during illumination becomes less, too. An extreme example for this simultaneous change in k_0 and $k_s(t)$ was found with fuchsin: In this case I_2 even increased with increasing field strength.

6.4. The Influence of Iodide on the Time Dependence $I_2(t)$ of the SDF

The action of iodide can be explained by the following reaction scheme:

$$\begin{tikzcd}
{}^3D^* + D_{ad} \arrow[r] \arrow[dd, "+I^-"'] & D^{\dot{-}} \arrow[dd, "{+HSO_3^-,\ pH \lesssim 6}"'] & {+}D_{ad}^{\dot{+}} \arrow[dd, "+I^-"] & \text{or} \quad D_{ad}^{\dot{-}} + D^{\dot{+}} \\
 & & & \\
D & D & D_{ad} + I^{\cdot} \arrow[dr, "SO_3^{--}", "pH \gtrsim 6"'] & \\
 & & & I^-
\end{tikzcd} \tag{27}$$

With iodide either the triplet state of weakly adsorbed dye molecules, ${}^3D^*$, is quenched or the lifetime of the radical ion $D_{ad}^{\dot{+}}$ is shortened. In all experiments with iodide $NaHSO_3$ was present. $NaHSO_3$ had a double function: at pH ≈ 6 it is an oxidant for $D^{\dot{-}}$ and a reductant for iodine. The reaction $D^{\dot{+}} + I^- \rightarrow D + I^{\cdot}$ has been shown by Kepka and Grossweiner(25) to occur in the eosin-sensitized photo-oxidation of iodide.

7. Sensitized Electron Injection

With rhodamine B(12) and eosin Y(14) also a weak sensitized electron injection i_- has been found. In this Section some new results obtained with erythrosin are presented and an explanation for sensitized electron injection is proposed.

In Fig. 11 the time dependences $I_2(t)$ of SDF, $I_{645}(t)$ of the luminescence of dissolved erythrosin and $i_-(t)$ of the sensitized electron injection are shown.

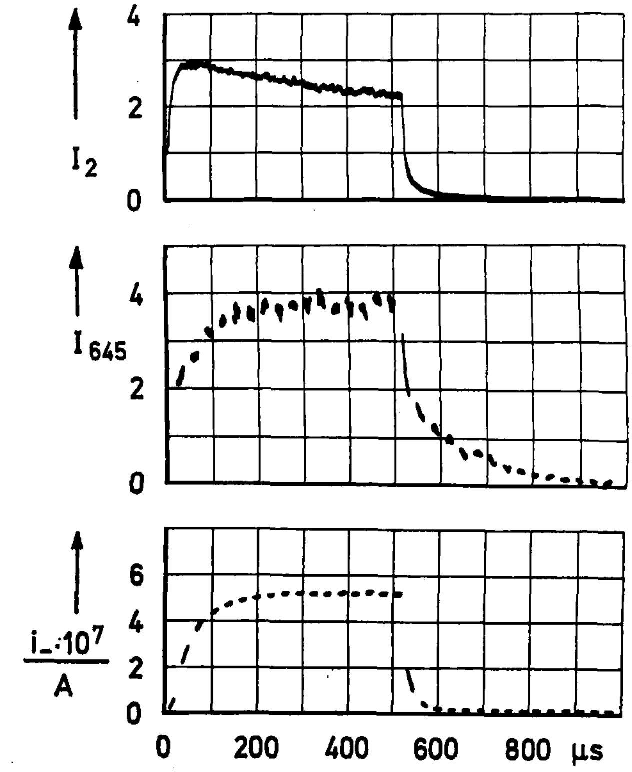


Figure 11. SDF I_2, fluorescence + phosphorescence of dissolved erythrosin, I_{645}, and sensitized electron injection i_-. $1.6 \cdot 10^{-6}$ M erythrosin, 10^{-2} M NaOH, 1 M KCl. Crystal thickness 34 μ, -1100 V, $I_0 \approx 1.0 \cdot 10^{19}$ photons cm^{-2} sec^{-1}, $\lambda = 514$ nm. Lifetime of triplet excitons 7 ms. The same result was obtained in the presence of Na_2SO_3 up to 0.1 M.

The decrease of I_2 during illumination is probably caused by an increase of k_s due to the occurrence of reaction (24). A "stationary" state is reached about 400 μs after the beginning of the excitation.

I_{645} was measured with a Schott red filter RG 645 (2 mm) which absorbed the main part of the fluorescence of erythrosin. In the stationary state the emission was composed in approximately equal parts of the fluorescence and the phosphorescence of the dissolved dye. From the decay of I_{645} the phosphorescence lifetime τ_{Ph} was determined: $\tau_{\mathrm{Ph}} = 140\ \mu$s. In an additional experiment (not shown in Fig. 11) the fluorescence intensity alone was measured and was found to be lower in the stationary state by a factor 0.73 than at the beginning of the excitation, i.e. in the stationary state 27% of the dye was not in the ground state. Assuming, that the dye was in the triplet state, the intersystem crossing quantum yield η_{T} could be calculated. With the excitation intensity $I_0 = 1.66 \cdot 10^{-5}$ Einstein $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$ and $\epsilon_n = 2.3 \cdot 7 \cdot 10^7\ \mathrm{Mol}^{-1}\,\mathrm{cm}^2$ at 514 nm it was found $\eta_{\mathrm{T}} = 0.98 \pm 0.10$. This method is similar to that used by Bowers and Porter,(26) who determined the depletion of the ground state and the triplet-lifetime by absorption measurements and obtained $\eta_{\mathrm{T}} = 1.07 \pm 0.13$.

The electron injection current i_- was delayed. The rise of i_- followed approximately the relatively slow rise of I_{645}, the decay of i_- followed approximately the relatively fast decay of I_2.

This behaviour is most simply explained by the assumption that triplet excitons are quenched at the surface by an electron donor Y. With the concentrations $n(0,t)$ of the triplet excitons and $c_y(t)$ of Y the electron injection current i_- is expected to be

$$i_-(t) \propto n(0,t) \cdot c_y(t)$$

As the rise of i_- is much slower than the rise of I_2, the electron donor Y is formed during the illumination. The nearly identical rise of I_{645} and i_- suggests that Y is formed by a reaction of ${}^3D^*$. i_- was found to be nearly independent of the concentration of Na_2SO_3, and also the phosphorescence lifetime was unaffected by Na_2SO_3. Thus the reactions

$${}^3A^* + SO_3^{--} \rightarrow A^{\overline{\cdot}} + SO_3^{\overline{\cdot}}$$

and

$${}^3D^* + SO_3^{--} \rightarrow D^{\overline{\cdot}} + SO_3^{\overline{\cdot}}$$

can be ruled out.

Probably Y can be identified with $D^{\overline{\cdot}}$, formed by the Lindqvist reaction.(24) The phosphorescence was completely quenched by 10^{-2} M ascorbic acid (R) and i_- was increased by a factor 3 in the stationary state. I_2 was not affected by the addition of ascorbic acid. In this case, $D^{\dot{-}}$ is certainly formed by the reaction(24)

$$^{3}D^{*} + R \rightarrow D^{\dot{-}} + R^{\dot{+}}.$$

According to this interpretation the sensitized injection of electrons is a two-photon process, which can be neglected at low excitation intensities. The observation of a delayed sensitized electron injection supports the explanation of the time dependence of the SDF in Sec. 6.3.

8. Discussion

8.1. ESSENTIAL RESULTS

The following results may be regarded as reliable:

(a) Free holes, observed as a sensitized hole injection current i_+ with rhodamine B, are predominantly generated by the primary CT-Qu. $^{1}D^{*} + A \rightarrow D^{\dot{-}} + A^{\dot{+}}$, if the following conditions are fulfilled: low dye concentration, field strength $> 10^5$ V/cm, and no strong oxidant X_2 present.

(b) The sensitized generation of triplet excitons is caused by two different mechanisms (see Fig. 2, (4), (5) and (6), (7′)).

(c) The unusual time dependence $I_2(t)$ of the SDF is caused mainly by the increase of surface quenching of triplet excitons during illumination.

(d) The dye sensitized injection of electrons is a delayed process.

There are still many open questions. This discussion will be limited to a few of them.

8.2. IMPORTANCE OF TWO-PHOTON PROCESSES

In the preceding sections several examples of two-photon processes have been given. The most directly observable processes are T-T-annihilation and the quenching of triplet excitons by an electron donor Y, probably $D^{\dot{-}}$, which is formed in a photoreaction. The corresponding measurable quantities, I_2 and i_-, have been found to be delayed. A further characteristic of these quantities should be that they are in general not proportional to the excitation intensity I_0. This requires further investigation. The intensity dependence of I_2 is investigated in detail in the following paper.(27)

Other two-photon processes are conceivable, e.g. the absorption of light by the intermediates D^{+} or D^{-} and two-photon absorption.

Of course two-photon processes are typical only for high excitation intensities. They can be neglected if one measures one-photon processes at low excitation intensities, e.g. a sensitized hole injection current. If, however, the measurable quantity depends on a two-photon process, as e.g. the SDF, then there does not necessarily exist an intensity region where the two-photon process of interest is still measurable but other two-photon processes can be neglected. For this reason an understanding of all possible two-photon processes is essential for the quantitative understanding of the SDF.

8.3. SENSITIZED HOLE INJECTION IN THE PRESENCE OF A STRONG OXIDANT X_2

The two proposed mechanisms of sensitized hole injection are compared in Fig. 12. The two mechanisms are abbreviated here to CT and ET-CT.

In the absence of an oxidant X_2 and with no voltage applied,

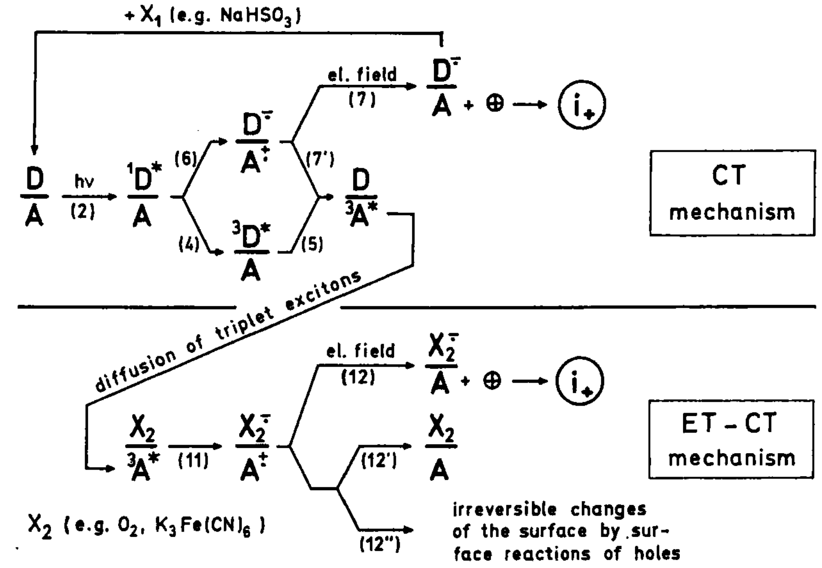


Figure 12. Comparison of the CT-mechanism and the ET-CT-mechanism of sensitized hole injection i_{+}. Fat horizontal lines represent the surface of the anthracene single crystal.

primarily injected holes (6) recombine with $D^{\dot{-}}$ and triplet excitons are formed (7′). At least at low excitation intensities the majority of triplet excitons produced at the surface is also quenched at the surface.(27) The nature of the quenching process is not at all clear. There is no indication that this quenching is predominantly CT-quenching. Possibly the inverse T-T-ET $D + {}^3A^* \rightarrow {}^3D^* + A$ and the deactivation of ${}^3D^*$ is an explanation(28) of surface quenching of triplet excitons. In homogeneous solution this inverse T-T-ET is known.(5c) If this explanation were correct one should find a decreasing surface quenching of triplet excitons with increasing triplet energy of the dye.

Experimentally one finds no irreversible change of the surface caused by surface quenching of triplet excitons (see, however, Sec. 2.3(d)).

In the presence of a strong oxidant X_2, e.g. of oxygen or $K_3Fe(CN)_6$, most triplet excitons are quenched by X_2 by a CT-process (11) as has been shown by Michel-Beyerle and Willig.(13) The recombination (12′) seems to be a relatively slow process (compared with (7′)). Other reactions (12″) of $A^{\dot{+}}$, which result in an *irreversible* oxidation of anthracene, can compete with (12′). Experimentally this is seen in the following way:(29) The intensity I_2 of SDF is decreased by the CT-Qu. (11). If the holes, generated thereby, are drawn into the crystal by an applied voltage, irreversible surface reactions of free holes are avoided and I_2 decreases only slowly at constant excitation. Lowering the applied voltage has two effects: A sudden increase of I_2 followed by a faster decrease of I_2. The sudden increase of I_2 is probably caused by the sudden increase of the generation of triplet excitons by the recombination (7′). The more rapid decrease of I_2 is certainly due to an increase of the rate of irreversible reactions (12″). This reasoning is based on the work of Mehl and coworkers.(30) In the presence of X_2 the measurement of a current voltage curve $i_+(V)$, which refers to a definite state of the crystal surface, is difficult if possible at all. Normally one is forced to limit experiments to the saturation current range.(13)

8.4. VOLTAGE DEPENDENCE OF THE MECHANISM OF SENSITIZED HOLE INJECTION IN THE PRESENCE OF A STRONG OXIDANT

Mulder(11) has found that normally no limiting current $i_{+\infty}$ of sensitized hole injection can be reached. Extrapolation of i_+ to infinite voltage ($i_{+\infty}$) shows, that a field strength $> 10^6$ V cm^{-1} is necessary in order that $i_+ \approx i_{+\infty}$. Michel-Beyerle and Willig[13] have found for the hole injection by CT-Qu. (11) of triplet excitons with X_2 = oxygen or $K_3Fe(CN)_6$ a current saturation already with $2 \cdot 10^4$ V cm^{-1}.

Kallmann and Pope[31] showed that the voltage dependence $i_+(V)$ at high field strengths may be mainly determined by the recombination velocity v of injected holes. Near the contact the force acting on an injected hole is due to two components: To the homogeneous field created by the applied voltage, and to the opposite image force exerted on the hole from the contact. Superposition of both results in a potential barrier near the surface. The authors give the following example: For 10^4 V cm^{-1} (applied voltage) the height of the barrier is 0.2 eV. The distance of the maximum of the barrier from the surface is ~ 100 Å. The probability of barrier penetration depends on the lifetime of the injected holes, i.e. on the recombination velocity v.

According to Kallmann and Pope[31] the initial excess energy of an injected hole is not essential for barrier penetration because it is quickly dissipated. Furthermore, in the case of hole injection by reaction (6) the excess energy must be small as is to be seen from the energy diagram in Fig. 1.

The quite different field dependence observed with the two mechanisms of sensitized hole injection may be explained by the assumption that reaction (7′) is much faster than the reactions (12′) and (12″). This has an interesting consequence, if also in the presence of X_2 the dominating reaction of $^1D^*$ is the CT-Qu. (6) and if triplet excitons are formed predominantly by (7′). In this case in the region of field strength $2 \cdot 10^4$ to $5 \cdot 10^5$ V cm^{-1} under a nearly constant current i_+ a continuous transition from the ET-CT mechanism to the CT mechanism may be hidden.

Thus primary injected holes have to be distinguished from secondary injected holes or, in other words, the primary CT-process is not necessarily the CT-process by which the charge carriers, measured as a photocurrent, are formed.

A further question is whether holes, produced by CT-Qu. (6), can be regarded as free holes at all. At least at low excitation intensities these holes are expected to be correlated to the semiquinone radicals $D^{\dot{-}}$.

Acknowledgements

I wish to express my gratitude to Prof. A. Weller for suggesting this research topic, for generous support of this work and for stimulating discussions.

I wish to thank Dr. Uta Nickel for her assistance in this work.

REFERENCES

1. Reviews: (*a*) Gutmann, F. and Lyons, L. E., *Organic Semiconductors*, Wiley, New York, 1967. (*b*) Bauser, H., " Lichtelektrische Leitung in Anthracen-Kristallen " *Naturwiss.* **54,** 505 (1967). (*c*) Le Blanc, O. H., Jr., " Conductivity ", in Fox, D., Labes, M. M. and Weissberger, A., eds., *Physics and Chemistry of the Organic Solid State*, Vol. 3, Interscience, New York, 1967, Chapter 3. (*d*) Bourdon, J. and Schnuriger, B., " Photosensitization of Organic Solids ", ibid., Chapter 2. (*e*) Helfrich, W., " Space-charge-limited and Volume-controlled Currents in Organic Solids ", ibid., Chapter 1.
2. Avakian, P. and Merrifield, R. E., *Mol. Cryst.* **5,** 37 (1968).
3. Pope, M., *Mol. Cryst.* **4,** 183 (1968).
4. Chambers, R. W. and Kearns, D. R., *Photochem. Photobiol.* **10,** 215 (1969).
5. (*a*) Parker, C. A. and Hatchard, C. G., *Proc. Chem. Soc. 1962*, 386; (*b*) Parker, C. A., *Advances in Photochemistry* **2,** 373 (1964); (*c*) Kikuchi, K., Kokubun, H. and Koizumi, M., *Z. Physik. Chem. N.F.* **62,** 75 (1968); *Bull. Chem. Soc. Jap.* **43,** 2732 (1970).
6. Steketee, J. W. and de Jonge, J., *Proc. Kon. Ned. Akad. Wet. Ser.* **B66,** 76 (1963).
7. Kallmann, H. and Pope, M., *Rev. Sci. Instr.* **30,** 44 (1959).
8. Mulder, B. J. and de Jonge, J., *Proc. Kon. Ned. Akad. Wet. Ser.* **B66,** 303 (1963).
9. Mulder, B. J., *Philips Res. Repts* **22,** 142 (1967).
10. Mulder, B. J., " Diffusion and surface reactions of singlet excitons in anthracene " (Thesis), *Philips Res. Repts Suppl.* 1968, No. 4.
11. Mulder, B. J., *Philips Res. Repts* **22,** 553 (1967).
12. Nickel, B., Staerk, H. and Weller, A., *Chem. Phys. Letters* **4,** 27 (1969).
13. Michel-Beyerle, M. E. and Willig, F., *Chem. Phys. Letters* **5,** 281 (1970).
14. Nickel, B., *Ber. Bunsenges. Physik. Chem.* **74,** 938 (1970)—abstract.
15. Nickel, B. and Maxdorf, H., *Chem. Phys. Letters* **9,** 555 (1971).
16. Suna, A., *Phys. Rev.* **B1,** 1716 (1970).
17. Nickel, B., *Ber. Bunsenges. Physik. Chem.* **75,** 795 (1971). In this paper the symbol $\Phi_2(\tilde{\nu})$ has been used for the excitation spectrum $k_0(\tilde{\nu})$ of sensitized generation of triplet excitons.
18. Lupien, Y. and Williams, D. F., *Mol. Cryst.* **5,** 1 (1968).
19. Kallmann, H. and Pope, M., *Rev. Sci. Instr.* **29,** 993 (1958); Cobas, A., Chalverus, J., Szmant, H. H., Trester, S. and Weisz, S. Z., *Rev. Sci. Instr.* **37,** 232 (1966).

20. *Gmelins Handbuch der anorganischen Chemie*, 8th ed., Schwefel Teil B, Lieferung 1–2, System Nr. 9, Verlag Chemie, Weinheim 1960, p. 431.
21. Schwabe, K., *Polarographie und chemische Konstitution organischer Verbindungen*, Akademie-Verlag, Berlin 1957, p. 196, No. 46.
22. Maxdorf, H., *Diplomarbeit*, Goettingen 1971.
23. Leonhard, H. and Weller, A., *Z. Physik. Chem. N.F.* **29**, 277 (1961); *Ber. Bunsenges. Physik. Chem.* **67**, 791 (1963); Weller, A. and Zachariasse, K., *J. Chem. Phys.* **46**, 4984 (1967); Grellmann, K. H., Watkins, A. R. and Weller, A., *J. Luminesc.* **1**, 678 (1970).
24. Lindqvist, L., *Arkiv för Kemi* **16**, 79 (1960); Kasche, V. and Lindqvist, L., *Photochem. Photobiol.* **4**, 923 (1965).
25. Kepka, A. G. and Grossweiner, L. J., Abstracts of the 6th international conference on photochemistry, Bordeaux, 6–8 Sept. 1971, No. 36.
26. Bowers, P. G. and Porter, G., *Proc. Royal Soc.* **299**, 348 (1967).
27. Nickel, B., *Mol. Cryst. and Liq. Cryst.* **18**, 263 (1972).
28. Willig, F., private communication.
29. Nickel, B., unpublished results.
30. Lohmann, F. and Mehl, W., *Ber. Bunsenges. Physik. Chem.* **71**, 493 (1967); Mehl, W. and Hale, J. M., " Insulator Electrode Reactions " in *Advances in Electrochemistry and Electrochemical Engineering*, Vol. **6**, 399 (1967).
31. Kallmann, H. P. and Pope, M., *J. Chem. Phys.* **36**, 2482 (1962).