

The Influence of Recombination between Holes and Reduced Redox Ions on the Efficiency of Hole Injection from Electrolytic Contacts into Organic Insulator Crystals

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The efficiency of hole injection from electrolytic contacts into organic insulator crystals is controlled by hole generation and hole destruction at the crystal surface through oxidized and reduced redox ions respectively and by hole escape into the crystal bulk which competes with hole destruction. By increasing the concentration of reduced redox ions from virtually zero in a suitable system the transition has been studied from the one extreme case where all the generated holes contribute to the injection current to the other extreme case where the majority of the generated holes recombines with reduced redox ions before they can escape into the crystal bulk. From the experiments one can deduce that the generated hole spends less than 10^{-10} s within the reaction distance of its reduced parent redox ion, at external field strengths $\geq 10^4$ V/cm, but returns to the crystal surface during a much longer time, e. g. during about 10^{-8} s at an external field strength of 10^5 V/cm, before it can escape finally into the crystal bulk.

I. Introduction

Recently we have described an experimental technique which prevents side reactions and thus allows for the measurement of an injection current originating at the virgin surface of an organic crystal in contact with an electrolytic solution¹. In a number of systems we have observed actual hole saturation currents where every hole which is generated at the crystal surface contributes to the current flow through the external circuit.

From the valence band of an organic crystal electrons can be transferred only to such oxidized redox ions which have shifted their empty electronic level to the energetic position of the valence band. This shift in the energy of the electronic level of the redox ion is brought about by a fluctuation in the bond-lengths and bond-angles of the ligands and in the orientation of its solvent environment. For a given concentration of oxidized redox ions at the crystal surface the probability for this "activation process" determines the number of holes which are generated per unit time at the crystal surface and therefore also the magnitude of the saturation current. Thus, from the magnitude of the saturation current one can determine directly the rate constant for the electron transfer reaction between the organic crystal and the oxidized redox ion^{2,3}. As is well known from electron transfer theory the rate constant depends on the potential drop over the

reaction distance leading to a slight increase of the saturation current with rising external field strength¹.

The observation of hole saturation currents in organic crystals is feasible since the aqueous solvent itself does not offer electrons at the energies of the valence bands in the organic insulator crystals. However, in analogy to the generation of a hole through an oxidized redox ion the hole can be destroyed through a reduced redox ion which has shifted its occupied electronic level to the position of the valence band through a suitable fluctuation. Thus, even when side reactions can be prevented we cannot expect to observe the saturation current for hole generation with every type of electrolytic contact. In the present paper we want to show experiments which demonstrate the influence of recombination between holes and reduced redox ions on the injection currents in organic crystals.

II. Experimental

The technique which has been used for the experiments in this paper has been described in detail elsewhere¹. The procedure is in short the following: For each measurement the hole injecting electrolytic solution is dropped from a pipette onto the virgin surface of a freshly grown crystal. The connections to the high voltage supply are arranged in such a way that the solution switches on an external field strength of e. g. 10^5 V/cm when touching for the first time the virgin crystal surface. This procedure is necessary to prevent a deterioration of the crystal surface due to slow side reactions of the generated

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holes with solvent molecules prior to the measurement of the injection current. Depending on the time resolution and its magnitude, the current is measured with an oscilloscope or electrometer. The anthracene and perylene crystals used for the measurements were grown from solution with a typical thickness of 10–20 μm and had triplet exciton lifetimes of 5 ms and 0.3 ms respectively.

III. Experimental Results

Before we discuss the experiments, we like to make a remark on the role of traps. Traps which are located in the crystal bulk have no influence on the stationary contact controlled injection current, since for every hole which is captured another hole is released. As long as the concentration of surface and impurity states in the band gap remains small as compared to the density of states in the valence band, we can also neglect thermally activated hole injection via electronic levels in the band gap. The trapping of a generated hole at the surface can enhance its time of residence at the surface and also its probability of recombination. We have found the dependence of the recombination reaction on the position of the valence band as expected for the trap free case. Therefore, the traps at our crystal surface must be so shallow that we can neglect their existence in the following discussion.

We have shown in an earlier paper that beyond space charge limitation the stationary injection current in an organic insulator crystal with an electrolytic contact can be formulated as follows¹:

$$J = J_s k_{\text{ES}} / (k_{\text{ES}} + C_{\text{Red}} k^{\text{Red}}) \quad (1)$$

with $J[\text{A/cm}^2]$ = injection current, $J_s[\text{A/cm}^2]$ = saturation current for hole generation, $k_{\text{ES}}[\text{cm/s}]$ = rate constant for the escape of a generated hole from the crystal surface into the crystal bulk, $C_{\text{Red}}[\text{cm}^{-3}]$ = concentration of reduced redox ions at the crystal surface, and $k^{\text{Red}}[\text{cm}^4/\text{s}]$ = rate constant for the destruction of a hole through a reduced redox ion at the crystal surface. The injection current J is thus determined by the number of holes generated per unit time at the crystal surface J_s/e , with e = elementary charge, and by the probability $k_{\text{ES}}/k_{\text{ES}} + C_{\text{Red}} k^{\text{Red}}$ for a generated hole to escape into the crystal bulk from recombination with a reduced redox ion. The steep increase of the rate constant k_{ES} with the applied electric field (compare below) is explained elsewhere with a quantitative

model describing the escape of the hole from an attractive Coulombic force due to its image charge and counter charge in the electrolytic solution⁴. The saturation current J_s is the direct measure for the rate constant k_{OX} of hole generation through an oxidized redox ion and can be formulated as follows¹:

$$J_s = e C_{\text{OX}} k_{\text{OX}} \quad (2)$$

with $C_{\text{OX}}[\text{cm}^{-3}]$ = concentration of oxidized redox ions at the crystal surface, $k_{\text{OX}} = k_{\text{OX}}^0 \times (1 + \gamma F)$ with $k_{\text{OX}}[\text{cm/s}]$ = rate constant for hole generation at zero external field strength, $\gamma[\text{cm/V}]$ = coefficient describing the dependence of the rate constant on the potential drop over the reaction distance due to the external field, and $F[\text{V/cm}]$ = external electric field, i.e. applied voltage divided by crystal thickness for sufficiently concentrated electrolytic solutions. By keeping the concentration of reduced redox ions C_{Red} sufficiently small, i.e. corresponding to $k_{\text{ES}} > C_{\text{Red}} k^{\text{Red}}$ in formula (1), we have measured the saturation current J_s and thus the rate constant k_{OX}^0 in a number of systems^{1, 3, 5}. The dependence of k_{OX} on the external field strength, i.e. the coefficient γ has been discussed in detail before¹ as also the dependence of C_{OX} on time when the consumption of the oxidized species is significant during the measuring time³.

In the following experiments we will show in a suitable system how the probability for hole escape $k_{\text{ES}}/k_{\text{ES}} + C_{\text{Red}} k^{\text{Red}}$ and thus the injection current J in formula (1) decreases with increasing concentration of the reduced redox ions C_{Red} . This effect can only be demonstrated when the rate constant for hole destruction k^{Red} is sufficiently large since a minimum value is required for the competing rate constant k_{ES} to leave the space charge limitation of the current voltage curve.

Firstly in Fig. 1a the hole saturation current in a perylene crystal is shown obtained with $10^{-2} \text{ N } [\text{Fe}(\text{CN})_6]^{3-}$ in the presence of 2 M K^+ and only a negligible concentration of reduced redox ions at the crystal surface. According to formula (2) this measurement yields a rate constant $k_{\text{OX}}^0 = 4 \times 10^{-4} \text{ cm/s}$ by extrapolating to zero applied field strength. The applied field strength is shown at the abscissa of Figures 1a–1c. The corresponding time dependent increase in the external field strength after contact formation at $t = 0$ is shown in Fig. 1d which is valid for all the three cases in Figures 1a–1c. The validity of the saturation condition $k_{\text{ES}} > C_{\text{Red}} k^{\text{Red}}$

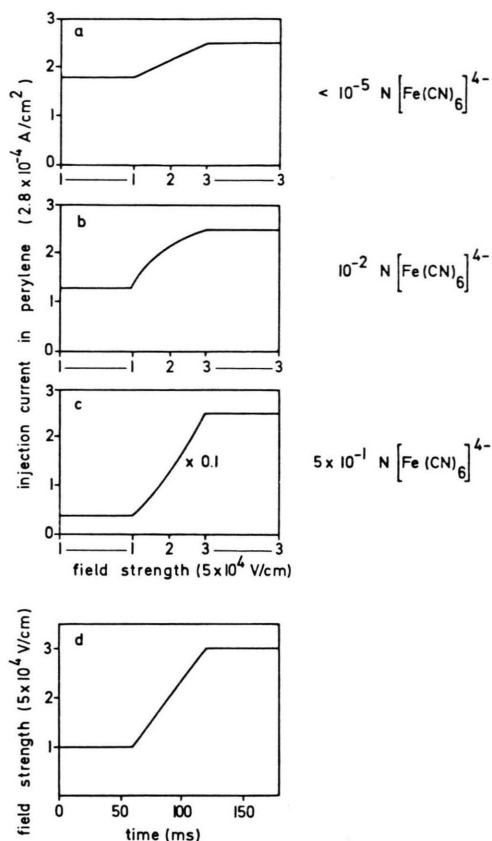


Fig. 1. Transition from the saturation current for hole generation in perylene (Fig. 1 a) through 10^{-2} N $[\text{Fe}(\text{CN})_6]^{3-}$ in 2 M KCl to much smaller injection currents dominated by recombination (Figs. 1 b and 1 c). The concentration of the reduced redox ions $[\text{Fe}(\text{CN})_6]^{4-}$ in the solution is indicated at the right hand side of the respective curve.

in the system has been checked further in the same range of field strengths through the measurement of an even larger but field strength independent saturation current which is controlled by the diffusion of oxidized redox ions towards the crystal surface^{1,3}. The observation of the saturation current excludes the occurrence of geminate recombination since every generated hole escapes from its reduced parent redox ion.

To check on the influence of non-geminate recombination between the generated holes and reduced redox ions other than their parent ions we have added to the solution additional reduced redox ions $[\text{Fe}(\text{CN})_6]^{4-}$. As shown in Fig. 1b the first clear decrease in the injection current was obtained when we added 10^{-2} N $[\text{Fe}(\text{CN})_6]^{4-}$. Naturally, every measurement was carried out at a freshly grown

crystal surface. We see in Fig. 1b that the initial injection current was only 70 per cent of the saturation current (Fig. 1a) at the same field strength $F = 5 \times 10^4$ V/cm but merged again with the saturation current for field strengths $F \geq 10^5$ V/cm. It is clear from formula (1) that the escape probability of a generated hole $k_{\text{ES}}/k_{\text{ES}} + C_{\text{Red}}k^{\text{Red}}$ increases from 0.7 to 1 in this range of field strengths in Figure 1b.

In Fig. 1c we have shown the same experiment with a solution containing 5×10^{-1} N $[\text{Fe}(\text{CN})_6]^{4-}$. Now the injection current was dramatically decreased as compared to the saturation current and remained 10 times smaller even at the external field strength $F = 5 \times 10^5$ V/cm. Obviously the escape probability was much smaller than 1 corresponding to the inequality $k_{\text{ES}} < C_{\text{Red}}k^{\text{Red}}$. The experiments shown in Figs. 1a – 1c have been carried out with constant concentration 2 M K^+ in the solution since cations increase the rate constant k_{OX} ⁵. The steep increase of the injection current with rising external field

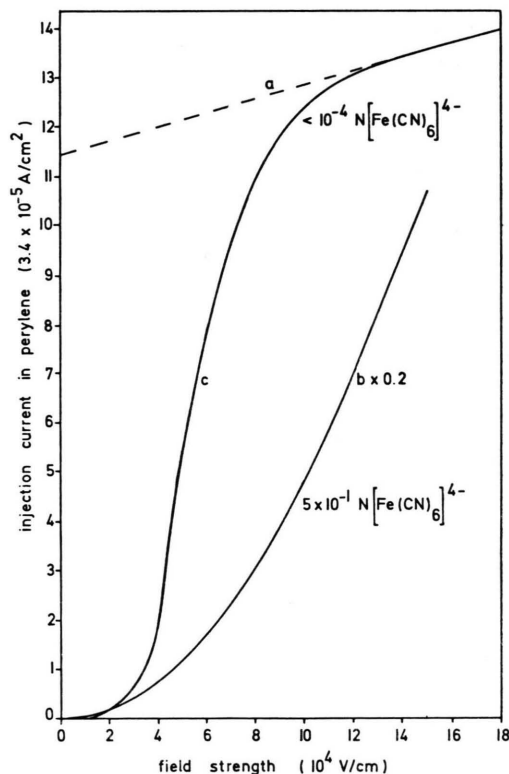


Fig. 2. Injection currents in perylene crystals with the same thickness (15μ) from the same batch. Curve a is the saturation current, curve c the space charge limited current, and curve b is the injection current dominated by recombination in the presence of 5×10^{-1} $[\text{Fe}(\text{CN})_6]^{4-}$.

strength in Fig. 1c obviously reflects the field strength dependence of the rate constant for hole escape k_{ES} .

In curve b of Fig. 2 we have plotted the field strength dependence of the injection current as in Fig. 1c over a wider range of field strengths. This latter measurement was recorded within 2.5 min after contact formation by raising the voltage from zero to 230 Volts. The measurement shown in Fig. 1c had been completed within 150 ms after contact formation starting already at a high field strength of 5×10^4 V/cm. The measurement in Fig. 2b allows for a comparison with the space charge limited current in the system shown in curve c of Fig. 2 and again with the saturation current and its extrapolation to zero applied field strength shown in curve a of Figure 2. The latter two have been measured at another perylene crystal from the same batch and with the same thickness of $15 \mu\text{m}$ when only oxidized redox ions were present in the solution as in the case of Figure 1a. Such curves have been reproduced neatly with crystals of the same thickness from the same batch. Fortunately, side reactions between holes in perylene and these solutions did not affect the measurements and are by orders of magnitude slower than those between holes in anthracene and a solution of ceric ions in e.g. $2 \text{ M H}_2\text{SO}_4$.

As will be shown in the discussion we expect a faster recombination reaction between $[\text{Fe}(\text{CN})_6]^{4-}$ and a hole in anthracene where the reaction should be even activation free. The occurrence of the saturation current in anthracene would show that the generated hole escapes from geminate recombination even in the activation free case at least in the range of field strengths where the saturation current is observed. With only $[\text{Fe}(\text{CN})_6]^{3-}$ and virtually no $[\text{Fe}(\text{CN})_6]^{4-}$ in the solution we have indeed observed the saturation current in anthracene as shown in Figure 3. Formula (2) yields the rate constant $k_{ox}^0 = 10^{-9}$ cm/s for hole generation in anthracene through $[\text{Fe}(\text{CN})_6]^{3-}$ in the presence of 4 M Li^+ .

A saturation current has been observed also for hole injection in anthracene through MnO_4^- in 0.5 M NaOH where the reduced redox ion again is expected to yield the activation free case for the recombination reaction. We can therefore conclude that at least in the range of field strength $F \geq 10^4$ V/cm the generated hole spends a shorter time within the reaction distance from its reduced parent redox ion than is characteristic for the activation

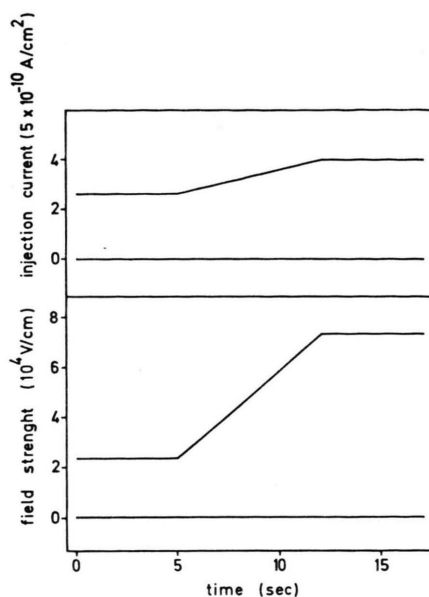


Fig. 3. Saturation current for hole generation in anthracene through $10^{-2} \text{ N } [\text{Fe}(\text{CN})_6]^{3-}$ in 4 M LiCl .

free recombination reaction. This characteristic time is represented by the preexponential frequency factor of the rate constant for electron transfer which is governed by a typical orientational or translational frequency usually estimated as 10^{10} to 10^{11} s^{-1} .

It appears of interest that the effect of geminate recombination on the injection current can be observed with redox ions which adsorb at the crystal surface. These experiments will be described elsewhere.

IV. Discussion

In the experiments described above we have found the influence of reduced redox ions on the injection current in accordance with formula (1). From these measurements we will now derive numerical estimates for the time during which the hole returns to the crystal surface before escaping finally into the crystal bulk and an upper limit for the total time the hole spends within the reaction distance from its reduced parent redox ion. These estimates will be obtained by using the measured rate constants k_{ox} and the standard free energy change for the reaction ΔG_{ox}^0 and a typical frequency factor for electron transfer reactions involving redox ions.

Firstly we can formulate the rate constant for hole destruction k_{Red} which corresponds to the measured rate constant for hole generation k_{ox} .

$$k_{Red} = k_{ox} \exp \{ \Delta G_{ox}^0 / kT \} \quad (3)$$

with

$$\Delta G_{\text{Ox}}^0 = I - E_{\text{RO}}^0 \quad (4)$$

where I = ionisation energy of the organic crystal and E_{RO}^0 = standard redox potential of the redox couple $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in the prevailing medium.

The rate constant k_{Red} in formula (3) is not yet the desired rate constant k^{Red} in formula (1) since the rate constant k_{Ox} refers to the reduction of the oxidized redox ion anywhere at the crystal surface whereas the rate constant k^{Red} implies the encounter of the reduced redox ion with just one individual hole at the crystal surface. We can obtain an estimate for the required normalization factor by assuming a value $C_{\text{Red}} k^{\text{Red}} \approx 10^5 \text{ cm/s}$ when there is firstly a fictitious solid state concentration of reduced redox ions at the crystal surface, e.g. $C_{\text{Red}} = 6 \text{ M} \triangleq 3.6 \times 10^{21} \text{ cm}^{-3}$, and secondly the recombination reaction is activation free for the hole, i. e. the hole can be reduced anywhere at the crystal surface. The numerical value of $C_{\text{Red}} k^{\text{Red}}$ in this case is of the order of the collision factor at a plain electrode. The relationship between k^{Red} in formula (1) and k_{Red} in formula (3) can thus be estimated as follows:

$$k^{\text{Red}} = k_{\text{Red}} \times 3 \times 10^{-22} \text{ cm}^4/\text{s}. \quad (5)$$

The absolute value of the rate constant for hole escape k_{ES} can be calculated for a given field strength from formula (1) by inserting the known values for C_{Red} , J , J_s and the value for k^{Red} determined from k_{Ox} and ΔG_{Ox}^0 with the help of Eqs. (3) and (5). ΔG_{Ox}^0 has been calculated from the ionisation energies $I = 5.36 \text{ eV}$ for perylene and $I = 5.83 \text{ eV}$ for anthracene and from the standard redox potentials 0.6 V (NHE) and 0.5 V (NHE) for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ in the presence of 4 M Li^+ and 2 M K^+ respectively⁵. For the recombination between the hole in perylene and $[\text{Fe}(\text{CN})_6]^{4-}$ in the presence of 2 M K^+ the results are $k^{\text{Red}} = 2.3 \times 10^{-19} \text{ cm}^4/\text{s}$ and $k_{\text{ES}} = 0.2 \text{ cm/s}$ at an external field strength $F = 2 \times 10^4 \text{ V/cm}$ increasing as curve b in Fig. 2 with rising field strength to the value $k_{\text{ES}} = 11 \text{ cm/s}$ at $F = 1.5 \times 10^5 \text{ V/cm}$.

An immediate survey of the connection between the rate constant for hole generation k_{Ox} and the rate constant for hole destruction k_{Red} can be obtained from the free energy plot of the electron transfer reactions. The experimental values of k_{Ox} determined with $[\text{Fe}(\text{CN})_6]^{3-}$ at perylene and anthracene are in good agreement with Marcus elec-

tron transfer theory⁶.

$$k_{\text{Ox}} = Z_{\text{Ox}} \exp \left\{ -\frac{w_{\text{R}}}{kT} \right\} \exp \left\{ -\frac{\Delta G^*}{kT} \right\} \quad (6)$$

with

$$\Delta G^* = \frac{1}{4} \lambda (1 + G_{\text{Ox}}^{0,\text{R}}/\lambda)^2$$

where $Z_{\text{Ox}} [\text{cm s}^{-1}]$ = effective collision factor, $w_{\text{R}} [\text{eV}]$ = reversible work to bring the oxidized redox ion from the bulk of the solution to the crystal surface, $\lambda [\text{eV}]$ = reorganization energy of the electron transfer reaction, $\Delta G_{\text{Ox}}^{0,\text{R}}$ = standard redox potential defined at the reaction distance as introduced by Marcus⁶. For a number of redox ions, e.g. also $[\text{Fe}(\text{CN})_6]^{3-}$, the experimental results show that the energy w_{R} is very small $< 0.05 \text{ eV}$ in this system and that $\Delta G_{\text{Ox}}^{0,\text{R}}$ can be determined within a margin of 0.1 eV simply from the ionisation energy of the organic crystal in the gas phase and the standard redox potential of the redox ion in the bulk of the solution⁵.

The agreement of the measured rate constants k_{Ox} with the quadratic dependence of the free activation energy ΔG^* on the standard free energy change $\Delta G_{\text{Ox}}^{0,\text{R}}$ has been reached in Fig. 4 by using the collision factor $Z_{\text{Ox}} = 10^4 \text{ cm s}^{-1}$ which is of the expected order of magnitude and the reorganization energy $\lambda = 0.8 \text{ eV}$ for the activation of $[\text{Fe}(\text{CN})_6]^{3-}$ at the crystal surface which is close to half of the value $\lambda_{\text{h}} = 1.4 \text{ eV}$ determined by Wahl and co-workers for the activation of both the oxidized and reduced redox ion in the homonuclear electron exchange reaction⁷. The free energy plot (Fig. 4) yields also the same estimate for the absolute gauge of the standard redox potential of the normal hydrogen electrode (NHE) as has been obtained with other methods⁸:

$$\text{OV (NHE)} \triangleq (4.5 \pm 0.1) \text{ eV (absolute)}. \quad (7)$$

The previously suspected disagreement of our experimental results with Marcus' formula (6)³ was due to the assumption of a wrong difference between the ionisation energies of perylene and anthracene which is actually 0.47 eV as used in Figure 4.

It is clear from Fig. 4 and formula (3) that a very small rate constant for hole generation k_{Ox} is linked to a very large rate constant for hole destruction k_{Red} and vice versa. Figure 4 explains why we expect an activation free recombination reaction between a hole in anthracene and $[\text{Fe}(\text{CN})_6]^{4-}$ in the presence of 4 M Li^+ whereas the reaction with the

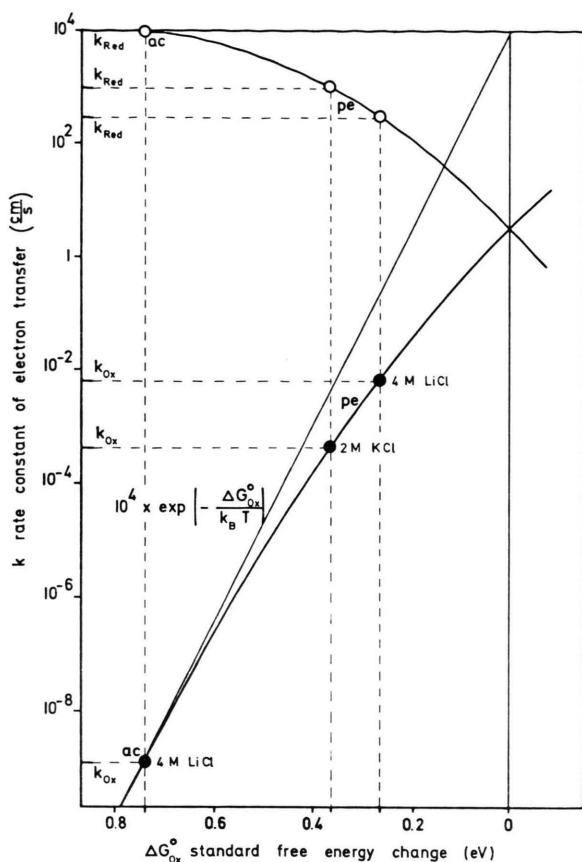


Fig. 4. Free energy plot of the logarithm of the rate constant for electron transfer k versus the standard free energy change of the reaction $\Delta G_{\text{ox}}^{\circ}$. The relationship between the measured rate constants for hole generation k_{ox} and the rate constants for hole destruction k_{Red} is indicated by the dashed lines in Fig. 4 for the experimental systems discussed in the text.

hole in perylene should be 13 times slower in the presence of 2 M K^+ . The absence of geminate recombination even in the case of the activation free reaction as is borne out by the experiment shown in Fig. 3 proves that the hole spends a shorter total time within the reaction distance from its reduced parent redox ion than corresponds to the reciprocal characteristic frequency of the activation free electron transfer reaction, usually taken as 10^{-10} to 10^{-11} s.

From hole escape in competition with non-geminate recombination as shown in Figs. 1c and 2b we can obtain an estimate of the distance which the generated hole travels parallel to the crystal surface before escaping into the crystal bulk. For $k_{\text{ES}} = C_{\text{Red}} k_{\text{Red}}$ in formula (1) the hole has equal probability to escape from or recombine with an activated reduced redox ion at the crystal surface. According to the above numerical value of $k_{\text{Red}} = 2.3 \times 10^{-19} \text{ cm}^4/\text{s}$ this situation is reached with a concentration $C_{\text{Red}} = 10^{-2} N \cong 6 \times 10^{18} \text{ cm}^{-3}$ of $[\text{Fe}(\text{CN})_6]^{4-}$ in 2 M KCl at the surface of perylene, at an applied field strength of $5 \times 10^4 \text{ V/cm}$. The average distance between two activated reduced redox ions is simply $(5 \times 10^{-8} \times C_{\text{Red}} \times 7.5 \times 10^{-2})^{-1/2}$ when the reaction distance is $d = 5 \text{ \AA}$ and $k_{\text{Red}} = 7.5 \times 10^{-2} k_{\text{max}}^{\text{Red}}$. Thus at an external field strength of $5 \times 10^4 \text{ V/cm}$ the hole travels within $d/k_{\text{ES}} = 5 \times 10^{-8} \text{ s}$ an average distance of about 350 \AA parallel to the crystal surface before it escapes into the crystal bulk.

Finally we like to make a remark on the thermodynamic situation in the system. Since the concentration of holes at the crystal surface q/e is much smaller than the density of states in the valence band $n \approx 10^{22} \text{ cm}^{-3}$ we can write¹:

$$q/e = k_{\text{ox}} C_{\text{ox}} / (k_{\text{Red}} C_{\text{Red}} + k_{\text{ES}}) \quad (8)$$

We have seen in formula (1) that the occurrence of the saturation current $J = J_s$ implies the inequality $k_{\text{ES}} > C_{\text{Red}} k_{\text{Red}}$ and thus a much smaller concentration of holes at the crystal surface q/e than corresponds to thermodynamic equilibrium between the organic crystal and the given composition of the electrolytic contact. In contrast when the recombination reaction dominates over hole escape, $k_{\text{ES}} < C_{\text{Red}} k_{\text{Red}}$ in formulas (1) and (8), the concentration of defect electrons at the crystal surface is virtually that of thermodynamic equilibrium between the organic crystal and the electrolytic contact.

Acknowledgement

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