# CHARGE-CARRIER INJECTION INTO HOMO-MOLECULAR CRYSTALS

## W. MEHL

*Orbisphere Corporation, 91 Route de la Capite, 1223 Cologny/Geneva, Switzerland*

### ABSTRACT

The properties of the interface between homomolecular crystals and electrolytes or metals is reviewed. Correlations between various experimental measurements and controllable parameters are predicted. The theoretical analysis is based on the assumption that the equilibrium potential difference at the contact interface is located within the solid and that the interaction is entirely electrostatic. Exceptions to this model are noted and tentative explanations are given.

## PROPERTIES OF THE INTERFACE BETWEEN A MOLECULAR CRYSTAL AND AN ELECTROLYTE

Equilibrium at the interface between a semiconductor and an electrolyte is characterized by the equality of the electrochemical potential of electrons (the Fermi level) on the two sides of the boundary plane which is established by a redistribution of charge resulting in the formation of an electrical double layer, an electronic charge in the solid being compensated by an excess of ionic charge in the electrolyte. In most molecular crystals so far investigated the concentration of intrinsic carriers seems to be very small indeed so that, upon contact with an electrolyte, equilibrium can be established only by modifying the carrier distribution in valence or conduction band to display accumulation of electrons in the former and of holes in the latter.

Recent work on the investigation of the carrier injection into anthracene crystals from metals and electrolytes[1] has shown that the electrostatic potential difference $\Delta\Phi$, at the interface, is in most cases determined by the difference of the Fermi levels for the two phases before contact, i.e. the interaction is entirely electrostatic and specific chemical interactions can be neglected:

$$\Delta\Phi = F_c - F_s \tag{1}$$

$F_c$ and $F_s$ denote the Fermi levels of the molecular crystal and of the electrolyte before contact, the sign of $\Delta\Phi$ denoting the sign of the charge on the semiconductor surface using the electrolyte as reference. All potentials refer to the charge free bulk of semiconductor and electrolyte, i.e. for electron injection $\Phi > 0$ in the semiconductor surface and $\Phi < 0$ in the electrolyte, while for

hole injection $\Phi < 0$ in the semiconductor surface and $\Phi > 0$ in the electrolyte.

The differential equations describing the space charge variations of the electrostatic field $E$ and the electrostatic potential at equilibrium are

$$dE/dx = 4\pi q e_0 n(x)/\kappa_M \tag{2}$$

$$d\Phi/dx = -E \tag{3}$$

$$dn/dx = \mu n E/qD \tag{4}$$

For simplicity a one-dimensional system was chosen. $n(x)$ is the density of carriers at the point $x$, $e_0$ is the magnitude of the electronic charge, $qe_0$ is the actual charge on each carrier and $\kappa_M$ is the permittivity of the crystal. The first equation is Poisson's equation in which the volume charge is due to injected carriers following the assumption that these are in large excess over the thermally generated carriers. Equation (3) expresses the field as a gradient of potential and equation (4) states that in the equilibrium case the diffusion of electrons away from the interface is balanced by the drift of electrons towards the contact. Solutions to the system of differential equations (2) to (4) with various boundary conditions have been given by several authors who may be consulted for details of the calculations[2, 3].

Lohmann[4] has given a solution for the case of an infinite solid with zero field at infinity on which a discussion of the potential distribution at the interface molecular crystal/electrolyte may be based. The interfacial potential distribution may be represented to a good approximation by the sum of three contributions

$$\Delta\Phi_T = \Delta\Phi_C + \Delta\Phi_H + \Delta\Phi_e \tag{5}$$

where $\Delta\Phi_c$ represents the space charge inside the semiconductor, $\Delta\Phi_H$ the potential difference across the inner Helmholtz layer, the region between the solid and the electrolyte into which ions do not penetrate unless there are specific chemisorption forces and $\Delta\Phi_e$, the potential difference across the diffuse double layer, the ionic space charge in the electrolyte formed by counter ions. Neglecting specific adsorption the potential gradient in the Helmholtz layer will be approximately constant, i.e. the potential difference $\Delta\Phi_H$ across the layer is determined by the field $E_H$ multiplied by the thickness of this layer.

Because of the continuity of the normal component of the displacement at the interface between crystal and electrolyte

$$\kappa_c \left(\frac{d\Phi}{dx}\right)_{x=0} = \kappa_H \left(\frac{d\Phi}{dx}\right)_{x_H > x > 0} \tag{6}$$

and the potential drop across the Helmholtz layer being thus

$$\Delta\Phi_H = \left(\frac{\kappa_c}{\kappa_H}\right) x_H \left(\frac{d\Phi}{dx}\right)_{x=0} \tag{7}$$

Lohmann[4] has derived from the system of differential equations (2) to (4) with the boundary condition $E \to 0$ for $x \to \infty$:

$$\left(\frac{\mathrm{d}\Phi}{\mathrm{d}x}\right)_{x=0} = (L_D^0)^{-1} \exp\left(-\frac{\overline{\Delta}_{n,p}}{2kT}\right) \tag{8}$$

where $L_D^0$ is a formal Debye length which would be observed for an insulator when all electrons in the valence band are released to the conduction band, assuming the density of states in both bands to be equal. $\overline{\Delta}_{n,p}$ represents the distance between carrier band and Fermi level at the crystal surface. From (7) and (8):

$$\Delta\Phi_H = \left(\frac{\kappa_c}{\kappa_H}\right)\left(\frac{qx_H}{L_D^0}\right)\exp_: \frac{-\overline{\Delta}_{n,p}}{2kT} \tag{9}$$

From (9) the potential drop across the Helmholtz layer has been calculated as a function of the distance between Fermi level and carrier band at the insulator surface at equilibrium (*Figure 1*) verifying the previously made and
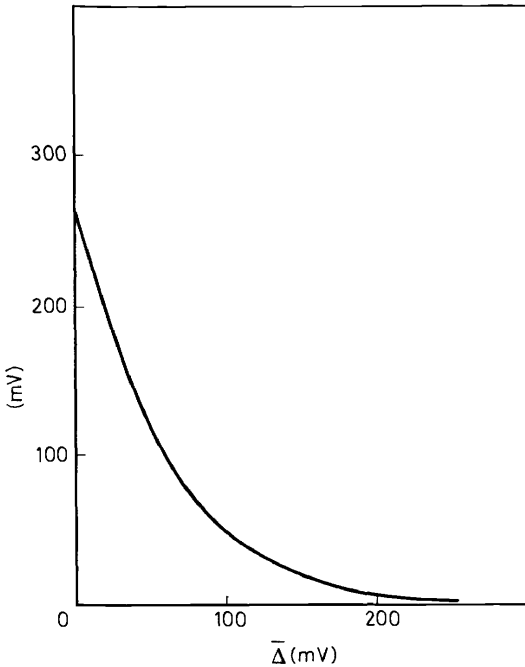


*Figure 1*. Potential drop across the Helmholtz layer as a function of the distance between Fermi level and carrier band at the crystal surface at equilibrium (Based on reference 4).

experimentally supported assumption that a sizeable potential drop across the Helmholtz layer can be expected only for the degenerate surface.

Unfortunately the direct experimental verification of the results of the preceding discussion is complicated by the extremely small carrier concentration in the bulk of the crystal. It was found that this difficulty can be overcome

when fairly strong oxidizing (or reducing) redox systems and extremely thin insulator films were chosen. The situation can then be realized when the thickness of the crystal is small compared to the Debye lengths of the two space charge layers which thus overlap so that the low intrinsic 'bulk' concentration of carriers does not materialize[6].

For simplicity we assume the contact at each insulator face to be established by the same redox electrolyte. The electrostatic potential has then a maximum at the centre of the crystal and a single solution to the boundary problem can be given by moving the origin of the coordinate system to the centre[5].

$$n(x) = n_c \sec^2 \left( \left\{ \frac{2\pi e_0^2 n_c}{kT} \right\}^{\frac{1}{2}} x \right) \tag{10}$$

$$\frac{e_0 \Phi(x)}{kT} = -2 \log \cos \left( \left\{ \frac{2\pi e_0^2 n_c}{kT} \right\}^{\frac{1}{2}} x \right) \tag{11}$$

where $n_c$ is the carrier density at the centre of the crystal (*Figure 2*).

Equations (10) and (11) describe the general principle only, because for a real crystal the free carrier density is, due to trapping effects, smaller than
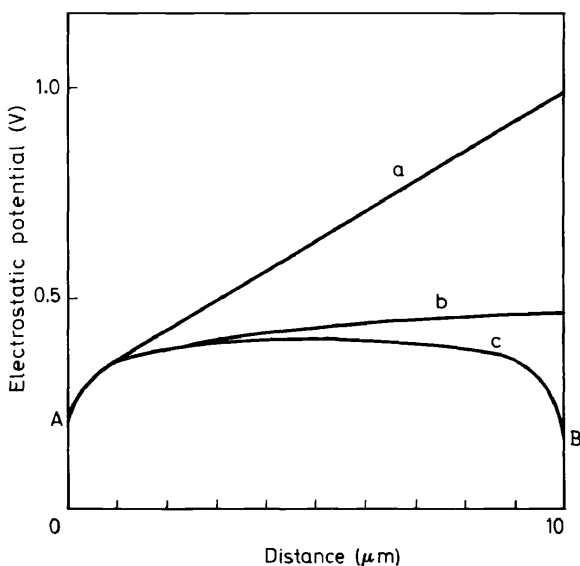


*Figure 2*. Variation of the electrostatic potential through a 10 μm thick insulator film sandwiched between two electrolytic contacts. At interface A the potential step is 0·1eV. At interface B the potential step is: 1eV for curve a (monotonic case), 0·472eV for curve b (intermediate case), 0·1eV for curve c (symmetrical case) (Based on reference 5).

equation (10) would suggest. Nevertheless it has been possible to measure reversible redox potentials at very thin anthracene membranes[6].

## ENERGETIC CONSIDERATIONS ON CARRIER GENERATION

As for molecular solids the lattice forces are of the van der Waals type there will be only small overlap between the orbitals of adjacent molecules. For anthracene e.g. the calculated intermolecular resonance integrals range in value from 5 to $30 \times 10^{-16}$ erg for nearest-neighbour pairs, depending on orientation[7]. Thus the energetics of carrier formation may be described in terms of localized electrons and holes[8], although the mobilities are probably best described in terms of the band approximation. Localized electrons and holes can be considered as negative and positive hydrocarbon ions respectively. The properties of these ions have been well investigated in solution[9] and, provided that the molecule is alternant, the spin and charge density distribution, apart from the sign of the latter, are identical for cations and ions. The frequencies of the excited electronic states, and excitation probabilities, are also independent of the sign of the charge. This simplifies the discussion of the properties of these ions.

The energy for formation of a hole or an electron can thus be calculated from either the ionization potential ($I$) of the molecule and the polarization energy $P_c^+$ or from the electron affinity ($A$) and the polarization energy $P_c^-$. As values for $I$ and $A$ have been determined experimentally[10] the remaining unknown quantities are the polarization terms.

The analogous polarization energies in liquid solution (differential real potentials) have recently been reported for a series of hydrocarbon positive and negative ions[11]. The solvent used was methyl cyanide. It was found that the polarization energies are identical for positive and negative ions of the same hydrocarbon. This implies that the solvent has the role simply of a dielectric medium for these large ions, and that there are no specific chemical solvation effects. It follows that a very good approximation to the polarization terms for these ions in another medium will be obtained by the use of the Born relationship to correct for the change in dielectric constant. Applying this to the case of ions in hydrocarbon crystals we have

$$P_c^\pm = P_s^\pm \frac{(\varepsilon_c - 1)\,\varepsilon_s}{(\varepsilon_s - 1)\,\varepsilon_c} \tag{12}$$

where the subscripts $c$ and $s$ refer to the crystal and solution respectively, and $\varepsilon$ is the dielectric constant.

In *Table 1*, the ionization potentials, electron affinities and ion polarization energies $P_s^\pm$ for $CH_3CN$ solution are listed for a series of alternant hydrocarbons. The dielectric constants of the crystals and the corresponding polarization energies $P_c^\pm$ calculated using equation (12) are also shown. In the last two columns of the table, the crystal ionization potential $I_c(=I + P_c^\pm)$ and the crystal electron affinity $A_c(=A - P_c^\pm)$ are recorded. We consider these crystals as intrinsic semiconductors and thus determine the energy of the Fermi level to be

$$F_c = \frac{I_c + A_c}{2} = 4.15 \text{ eV} \tag{12}$$

as the mean value for the hydrocarbons listed in *Table 1*. The constancy of the Fermi level is a consequence of the Pople–Hush rule of the constancy of

503

Table 1. Electrochemical properties† of some aromatic hydrocarbons (based on reference 8)

| Hydrocarbon | $I^a$ | $A^b$ | $-P_s^{\pm c}$ | $\varepsilon_c^d$ | $-P_c^{\pm}$ | $I_c$ | $A_c$ | $F_c$ |
|---|---|---|---|---|---|---|---|---|
| Naphthalene | 8.20 | 0.15 | | | 1.28 (42) | 6.92 | 1.43 | 4.18 |
| Anthracene | 7.61 | 0.55 | 1.94 | 3.38 | 1.74 (42) | 5.86 | 2.29 | |
| | | | | | 1.41 | 6.20 | 1.96 | 4.08 |
| Chrysene | 8.01 | 0.33 | 1.83 | 2.97 | 1.25 | 6.76 | 1.58 | 4.17 |
| Pyrene | 7.72 | 0.39 | 1.86 | 3.36 | 1.35 | 6.37 | 1.74 | 4.06 |
| Phenanthrene | 8.06 | 0.20 | 1.76 | 2.54 | 1.10 | 6.96 | 1.30 | 4.13 |
| 1,2 Benzanthracene | 7.74 | 0.46 | 1.86 | 3.41 | 1.35 | 6.39 | 1.81 | 4.10 |
| Triphenylene | 8.19 | 0.14 | 1.84 | 3.41 | 1.34 | 6.85 | 1.48 | 4.17 |

† Ionization potentials and electron affinities $(I, A)$ of hydrocarbons in the gas phase and in the crystal $(I_c, A_c)$. $P_s^{\pm}$ and $P_c^{\pm}$ are the polarization energies of ions in methyl cyanide solution and in the hydrocarbon crystal respectively. $\varepsilon_c$ is the dielectric constant of the crystal, $F_c$ is the energy of the Fermi level. The data for naphthalene crystal and for the first line for anthracene crystal were taken from reference (40). All energies are in eV.

a For sources of data see reference 11.

b See reference 12.

c See reference 11.

d Calculated from molecular polarizabilities using the method of Denbigh, Trans. Faraday Soc. 36, 936 (1940). Crystal densities are calculated from unit cell data of A. I. Kitaigorodskii, 'Organic Chemical Crystallography' (translated from Russian by Consultant Bureau, New York, 1963).

the sum of electron affinity and ionization energy for alternant hydro-carbons[13]. In *Table 1* an electron in vacuum at infinity has been used as the reference energy state. Conversion between energy levels measured on this reference system and those measured on the electrochemical scale may be achieved through use of energy on the vacuum scale of the origin of the hydrogen electrode scale which has been determined[14] to be

$$E_{H^+H_2} = -4.5 \, eV, \text{ so that } E^H = -4.5 - E.$$

## INJECTION OF CARRIERS FROM ELECTROLYTES

**Electrostatic Interaction**

The thermally generated intrinsic carrier density in homo–molecular crystals is so small that it is useful to think of these solids as perfect insulators. It is well known that a space charge limited current can be passed through an insulator if one of the contacts is 'ohmic'[2, 15]. In the ideal situation an ohmic contact provides an infinite reservoir of carriers just inside the surface of the solid from which a current can be injected into the bulk of the solid by an applied electric field. The magnitude of the current at any particular field strength will then be determined by the properties of the space charge in the solid which reflects the bulk properties of the crystal.

In real systems the current increases with the applied field until the surface reservoir of carriers is exhausted. With further increase in voltage the magnitude of the current is no longer controlled by the bulk properties of the solid but rather by the surface generation rate. Investigation of the deviation from the space charge limited current behaviour is profitable for the under-standing of the surface reaction which leads to carrier injection. Kinetically a dynamic exchange of carriers between the contact and the crystal takes place, the currents in both directions being identical at equilibrium. When the exchange is with an electrolyte solution containing a redox system we may write the surface reaction in the form

$$M + A^{\pm} \rightleftarrows M^{\pm} + A \tag{13}$$
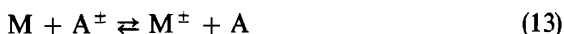
The electron or hole donor species in solution $A^{\pm}$ transfers a carrier to a molecule in the crystal, M, generating a carrier in the surface reservoir $M^{\pm}$ and an acceptor species A.

An electrolyte forms an ohmic contact to a crystal if there is a large concentration of carriers in the surface reservoir at equilibrium i.e. if the carrier band is bent in the vicinity of the Fermi level. On application of an electric field the surface reservoir will be emptied very quickly unless it is replenished by a sufficiently fast surface generation process. When the applied voltage is sufficiently high to reduce the surface concentration of carriers to zero the current becomes saturated, provided the applied field does not affect the surface reaction.

The limiting current is determined either by the rate of the charge transfer reaction, equation (13), which can thus be readily determined, or by the limiting diffusion rate of donor species to the solid/solution interface. This view has been confirmed experimentally by using as a model system anthra-

cene platelets which were sandwiched between two electrolyte contacts[1]. The passage of a continuous hole current through the crystal was possible if one of the contacts contained a redox system which was strongly oxidizing i.e. which has a sufficiently positive redox potential (European sign convention) and which has a high rate constant for the electron exchange reaction. Energetic balance is provided by the equality of the electrostatic work of injection and the chemical energy acquired in the donation reaction. Electron injection has also been observed when the analogous requirements, redox systems with sufficiently negative equilibrium potentials and fast exchange rate, were fulfilled[1]. A quantitative treatment of the model outlined above has been derived for the case when the electron transfer reaction is a member of the simplest class of redox reactions, for which the activation processes associated with the charge transfer reaction consist exclusively of rearrangement of the outer coordination sphere, change of the bond lengths in the inner coordination sphere and polarization of the crystal lattice, having only weak interactions between the orbitals of the solid and the species in the solution[1].

Detailed theoretical studies on such systems have been made by various authors who agree that in the first approximation the cross section through the potential energy surface made by the reaction coordinate is parabolic[16-18]. The reaction coordinate is frequently imagined to be the effective charge, which changes during the electron transfer process from the initial to the final state, on the species in the electrolyte.

Using these theories and the approximation that all of the potential difference in the interface is located within the solid it has been shown that the limiting injection current from redox systems is given by (1):

$$i_{lim} = ZFN_c[A^{\pm}] \exp\{-(\lambda/4RT)[1 + \overline{\Delta}/\lambda]^2\} \qquad (14)$$

A formula for $Z$ has been derived[19]; it is roughly $10^7$ cm$^4$mole$^{-1}$sec$^{-1}$. $N_c$ is the density of vacant states in the solid ($\sim 10^{20}$ cm$^{-3}$), $[A^{\pm}]$ the concentration of the donor species, $F$ the Faraday, $\lambda$ the energy parameter defining the reaction energy parabolas and $\overline{\Delta}$ the gap between carrier band and Fermi level at the crystal surface. Equation (14) shows that in order for a redox electrolyte to provide an ohmic contact $\lambda$ and $\overline{\Delta}$ must be small. The first condition is fulfilled if the homogeneous electron exchange rate for the redox system

$$A^{\pm} \rightleftharpoons A + qe_0 \qquad (15)$$

is fast. The energy gap at the crystal surface is determined by

$$\overline{\Delta} = \Delta - FV \qquad (16)$$

where $\Delta$ is the gap between carrier band and Fermi level in the bulk of the crystal and $V$ is the magnitude of the potential difference at equilibrium between the surface and the bulk of the solid. $V$ is linearly related to the redox potential $E_0$:

$$V \approx E_0 - E_{FB} \qquad (17)$$

Here $E_{FB}$ is the so called 'flat band potential' which is the equilibrium poten-

tial of a redox system for which, in contact with the crystal, the situation $V = 0$ is obtained. A large magnitude for $V$ requires that $E_0$ is well separated from $E_{FB}$ i.e. the redox system has to be either strongly oxidizing or strongly reducing.

## Specific Chemical Interaction between Crystal and Contact

In the preceding discussion it has been shown that charge carriers can be injected into molecular crystals if certain energetic conditions are fulfilled. Experimental evidence has shown that the realization of these conditions is a sufficient but not a necessary criterion for the electrolyte to form an injecting contact. Cases have been found for which electrolytes do not obey the electrostatic conditions discussed above yet permit carrier injection into molecular crystals on application of an electric field.

*Hydrogen Atom Transfer*

It has been shown that hydrocarbons can form proton complexes in which the proton is linked to one of the carbon atoms by a covalent bond[20]. The structure of protonated anthracene is probably
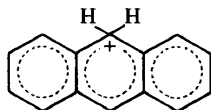


In homogeneous solutions protonated hydrocarbon molecules can donate hydrogen atoms to suitable H-acceptors with the formation of radical ions:

$$MH^+ + A_H \rightarrow M^+ + A_H H$$
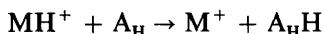
In this mechanism the rate of hydrogen atom transfer is proportional to the acidity function of the solvent medium. The identical reaction takes place if the protonated hydrocarbon molecules form the surfaces of the crystal. The radical ions then form a charge reservoir from which carriers can be injected into the bulk of the crystal under the influence of an applied electric field.

Hoffmann has shown[21] that oxygen and anthraquinone are very efficient H-acceptors in contact with an anthracene crystal with a protonated surface. He has found that for low voltages the current was determined by the space charge in transit through the crystal while for sufficiently high voltages a limiting current was observed which was determined by the rate of carrier generation at the crystal/solution interface. In the case of protonated anthracene crystals and oxygen or anthraquinone, carrier generation was limited by the rate of diffusion of these species to the crystal/solution interface. Under suitably chosen experimental conditions it should be possible to determine from the limiting injection current the rate of the hydrogen atom transfer reaction.

*Alkali Metal Complexes*

According to the electrostatic model a contact without an energy barrier

507

can be made to the valence band of a semiconductor for metals whose work function $\Phi$ is sufficiently large that $\Phi \geqq F + \Delta$, where $F$ is the energy of the Fermi level and $\Delta$ is the separation of Fermi level and valence band in the bulk of the crystal. As $F \approx -4.17$ eV and $\Delta \approx -1.9$ eV for metals[22] with $\Phi > 6$ eV, dark injection of holes can be expected and, following the equivalent argument, for metals with $\Phi < 2.3$ eV electron injection should be possible.

The latter value can be reached with alkali metals and from contacts consisting of either caesium or a sodium-potassium alloy dark injection in anthracene crystals was indeed observed[35,41]. The electrostatic argument presented above must, however, be accepted with great reservation only, because electron injection leading to a space charge limited current has also been found for Na-K alloy contacts to naphthalene crystals. For naphthalene $F = -4.17$ eV and $\Delta \approx 2.75$ eV, so that $\Phi \approx \leqq 1.6$ eV must be reached according to the electrostatic model before an 'ohmic' contact can be established while for the Na-K alloy the lowest value for $\Phi$ reported[23] is 2.0 eV.

A much more likely explanation for the injection mechanism of electrons into anthracene and naphthalene is a specific chemical reaction leading to the formation of radical ions. It is known that anthracene and naphthalene form, with alkali metals, compounds of the type [(alkali metal)$_n$(hydrocarbon)] with $1 \leqq n \leqq 2$. The properties of these compounds have been investigated by Ubbelohde and co-workers[24]. Their colour is deep blue and from density measurements it was concluded that e.g. for the compound [Na$_{1.7}$ Anthracene] the volume containing 1 mole of anthracene is 163.4 cm$^3$ which compares with 155.0 cm$^3$ per mole of pure anthracene. Indeed an expansion of the part of an anthracene crystal which was in contact with an Na-K alloy could be observed. Also, both for anthracene and naphthalene, the formation of an intensely blue coloured compound was observed in the contact area and ESR measurements showed the presence of radical ions[25].

We must thus conclude that the injection of electrons into anthracene and naphthalene crystals from alkali metals is the results of a chemical reaction which results in the formation of hydrocarbon radical ions which represent a reservoir of electrons.

Supporting this view Many[42] demonstrated, in a series of ingenious experiments, that at the interface between anthracene and an alkali or alkaline earth metal a single discrete set of traps is formed. The traps are 0.95 eV deep and are present with a density of about $10^{13}$ cm$^{-3}$. By optical excitation electrons can be injected from these traps into the conduction band of anthracene. Detrapping occurs by interaction of occupied traps with photons, triplet or singlet excitons. The traps are continuously filled by electron injection from the metal contact.

### Field Assisted Carrier Injection

Solutions of various redox systems have been found from which carriers can be injected in molecular crystals although energetic considerations exclude the 'outer sphere activated' electron transfer mechanism[1,21].

The best investigated example is the injection of holes into naphthalene crystals from a solution of ceric sulphate in 15 N sulphuric acid[25]. The standard redox potential for $Ce^{4+}/Ce^{3+}$ is $E_0^H = 1.45$ V and the level for the

naphthalene may be found at $E_v^H = 2\cdot3\text{–}2\cdot4$ V so that, following equation (14), no hole injection current into naphthalene crystals should be detectable. Nevertheless a significant hole current was measured. The current voltage curves showed several characteristic differences compared to the familar current-voltage curves measured with the same system on anthracene:

1. No saturation current was observed.
2. The current is smaller than the space charge limited current for the same field strength.
3. The current voltage curve is independent of the crystal thickness.
4. A change in the $Ce^{4+}$ concentration affected the total current voltage curve.

In particular, when the concentration of $Ce^{4+}$ changed while the applied voltage at the naphthalene crystal was kept constant, the current varied according to $i \backsim c^n$ with $0.45 \leqq n \leqq 0.6$.

The results prove that the current voltage curve is independent of the bulk properties of naphthalene in the total voltage range investigated. We must thus assume that the applied voltage decays partly across a surface layer which consists of a complex formed by the absorption of ceric ions at the naphthalene surface. The complex may be of the charge transfer type with naphthalene as electron donor and ceric ions as acceptor.

Complex formation between aromatic hydrocarbons and metal ions has been observed in the solid state hitherto for the systems[26] benzene/$Ag^+$ and[27] anthracene/$Ce^{4+}$. Measurement of the isotopic hydrogen exchange in the presence of platinum ions also indicates complex formation between aromatic hydrocarbons and platinum (II) ions[28]. Our assumption of complex formation between naphthalene and ceric ions is supported by ESR measurements which showed a signal with $g = 2.0043$ for a mixture of ceric sulphate and naphthalene. With this model the concentration dependence of the current at constant voltage reflects an adsorption isotherm for ceric ions which has the form of the Ostwald–Freundlich isotherm $c_{ads} = \alpha c^n$, $n < 1$. It is known that for intermediate degrees of coverage adsorption phenomena can frequently be described by an isotherm of this type[29].

During these experiments the highest applied field strength was $5 \times 10^5$ V/cm across the sample which may consist of naphthalene coated by a surface layer of the charge transfer complex. The potential difference in the surface layer can be estimated by means of the formula

$$E_S = \frac{\varepsilon_B}{\varepsilon_S} E_B$$

where $E_B$ is the field within the bulk of the sample and $E_S$ is that in the surface film; $\varepsilon_B$ is the dielectric constant of naphthalene and $\varepsilon_S$ is the corresponding quantity for the surface layer. Since $\varepsilon_S \simeq \varepsilon_B$ the field strength across the surface layer will be roughly the same as that across the sample. From the difference between the $Ce^{4+}/Ce^{3+}$ and Naph/$Naph^+$ (Naph and $Naph^+$ are the naphthalene molecule and positive ion) equilibrium potentials we can estimate that the energy for charge separation in a ceric-naphthalene charge transfer complex according to

$$(\text{Naph} \dots \text{Ce}^{4+}) \rightarrow (\text{Naph}^+ \dots \text{Ce}^{3+})$$
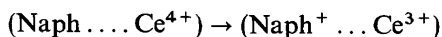
will be about 1eV. If we assume the distance between the charge centres to be about 5Å, we would need a field strength of $2 \times 10^7$ V/cm in order to obtain complete charge separation. This crude estimate shows that this effect is not a likely explanation for the current observed. A more complicated model may therefore be necessary.

## PHOTOINJECTION OF CARRIERS

### Electrolyte Contacts

According to the model of Kallmann and Pope[30] photoinjection of carriers into a single crystal of anthracene is caused by excitons which are generated by light absorption, diffuse to the surface and react here with electron donors or acceptors. The charges so generated can migrate through the crystal under the influence of an applied electric field. The maximum current which can pass through the interface is

$$i_{\text{lim}} = Fk_e[M^*] \tag{18}$$

where $F$ is the Faraday and $M^*$ is the density of excited molecules at the crystal surface. This has to be treated as a diffusion problem for excited species and a migration problem for carriers through the crystal with the kinetic equation for the interfacial reaction as a common boundary condition.

A solution for this problem has been given in the form[31]

$$\frac{i_{\text{lim}} - i_0}{Fe_0 I_0} = \Phi = f_1 f_2 \tag{19}$$

where

$$f_1 = 1/[1 + 1/(\varepsilon\sqrt{D\tau})] \tag{20}$$

and

$$f_2 = 1/[1 + 1/(k_e C_A^{\pm}\sqrt{\tau/D})] \tag{21}$$

Here $i_{\text{lim}}$ is the limiting photocurrent which can be observed at high enough applied voltages, $I_0$ is the light intensity, $i_0$ is the limiting value for the dark injection current, $\varepsilon$ is the absorption coefficient for the wavelength of the radiation used, $D$ is the diffusion coefficient and $\tau$ the mean life-time for excitons. $\Phi$ is the quantum efficiency for the electrochemical charge injection process which has been factorized into the efficiencies of collection of excitons by the surface, $f_1$, and the efficiency of the charge separation $f_2$. At small values of $f_2$, the measured current is linearly proportional to the concentration $C_A^{\pm}$ of the solution phase species. A quantitative discussion of $f_2$ is possible if the charge transfer reaction is of the outer sphere type for which we can apply the treatment of Marcus–Hush[16, 17].

We write the interface reaction in the form:

$$1_{M^*} + A^{\pm} \xrightarrow{k_e} M^{\pm} + A \tag{22}$$

The standard free energy change of this reaction is given by

$$\Delta F^* = \mu_M^{\circ\pm} + \mu_A^{\circ} - \mu_{1_{M^*}}^{\circ} - \mu_A^{\circ\pm} \tag{23}$$

For the same reaction with groundstate molecules we obtain

$$\Delta F = \mu_M^{\circ\pm} + \mu_A^{\circ} - \mu_M^{\circ} - \mu_A^{\circ\pm} \tag{24}$$

which can be expressed as [see equation (16)]

$$\Delta F = \overline{\Delta} \tag{25}$$

Thus

$$\Delta F^* - \Delta F = \mu_{M*}^{\circ} - \mu_M^{\circ} \tag{26}$$

If $E_x$ is the energy difference between the excited state and the ground state we obtain

$$\Delta F_p = \overline{\Delta} - E_x \tag{27}$$

so that [see reference (31)]

$$k_e = Z \exp\left\{\frac{-\lambda}{4RT}\left[1 + \frac{-E_x}{\lambda}\right]^2\right\} \tag{28}$$

Detailed experimental investigations of the mechanism of photoinjection into anthracene were made[32] with aqueous solutions of $Na_2IrCl_6$, $TlCl_3$ and $FeCl_3$. They showed a striking anomaly, namely that the rate of the photoinjection reaction with $IrCl_6^{2-}$ was of about the same order of magnitude as $Tl^{3+}$ or $Fe^{3+}$ while the dark injection reaction with $IrCl_6^{2-}$ was more than five orders of magnitude faster than with the other two ions.

It was found that for the hexaquoiron complexes the magnitude of the polarization energy change in solution associated with the charge transfer step was so small that an excited state of the reduced component was preferred as a product of the reaction, while a large polarization energy change for the thallium system rendered the ground state of the product most accessible for the reaction. It was shown that in the case of $IrCl_6^{2-}$ virtually all the energy of the excitons is transferred by resonance energy transfer. To prove this, the exciton diffusion problem was solved for simultaneous electron and energy transfer[33]. The result showed an unchanged collection efficiency for excitons while the efficiency of charge separation was now

$$f_2 = \frac{1}{1 + \dfrac{1}{k_e C_e \sqrt{(\tau/D)}} + \dfrac{k_Q C_Q}{k_e C_{A\pm}}} \tag{29}$$

where $k_Q$ is the rate constant for the energy transfer reaction and $C_Q$ the concentration of quenching species in solution. In the case of $IrCl_6^{2-}$ $C_Q = C_{A\pm}$.

The quenching rate constant was determined from (27) and compared with a value derived from the application of Förster's treatment[34] of resonance energy transfer upon quenching at the interface between solid and an electrolyte. For a $10^{-2}$ molar solution of $Na_2IrCl_6$ in ln HCl the experimental value was $k_Q = 2.05 \times 10^8$ $cm^4$ $mole^{-1}$ $sec^{-1}$ and the value derived from theory $k_Q = 3.9 \times 10^7 cm^4$ $mole^{-1}$ $sec^{-1}$.

## Excitation of the Contact

### Metallic Contact

While space charge limited electron currents in anthracene have been reported with alkali metal contacts[35], hole injection from metallic contact has proven to be difficult. Dark injection has been observed from evaporated gold[35] and selenium[36] contacts, but the exact mechanism is in doubt; it seems to be a poorly reproducible field assisted process.

Williams and Dresner[37] have shown that for metals with $\Phi < E_V$ hole injection is still possible if the missing energy $E_V - \Phi$ is supplied by light. The authors irradiated a contact through the anthracene crystal with light of variable wavelength and measured the photocurrent passing through the crystal under an applied electric field. On plotting the photocurrent against the square root of the wavelength a straight line relationship was found from which, by extrapolation, they determined the lower limit $E_{lim}$ of the light energy for photoinjection of holes. For gold, silver, aluminium, lead and magnesium they found

$$\Phi \, (\text{metal}) + E_{lim} \, (\text{metal}) = E_V \, (\text{anthracene})$$

where $E_V = 5.8 \pm 0.34$ eV which is in good agreement with $E_V \approx 6$ eV determined from electrochemical data[14]. For the metals mentioned the interaction at the interface metal/anthracene is thus entirely electrostatic i.e. specific chemical interactions could be neglected.

The detailed analysis of the spectral response of the photoinjection current showed a very complex structure which reflected the structure of the valence band. The valence band was shown to be split into many well defined bands, separated from each other by the energy of a vibrational quantum. Interaction between the electron states at the Fermi level of the metal and any level of the valence band is possible.

### Electrolytic Contact

Injection from excited species in the electrolyte is difficult to achieve because the lifetime of singlet states is so short that electron transfer cannot compete with transfer to the groundstate and the absorption coefficient for triplet excitation is usually so small that the concentration of excited states is too low to be noticeable. Fortunately there is at least one exception: the visible absorption of the iodine molecule (near 520 m$\mu$) arises mostly from transitions between the ground state $^1\Sigma^+$ and the excited state $^3\Pi^+$. The radiative lifetime of the transition $^3\Pi^+ \to {}^1\Sigma^+$ has recently been determined[38] to be $(7.2 \pm 1.0) \times 10^{-7}$ sec.

An iodine solution was illuminated through the anthracene crystal and the photocurrent measured[39]. The spectral response of the current closely resembled the absorption spectrum of iodine. The exciton diffusion model, which was used to analyse the case of charge injection through electron transfer reaction with excitons, could be applied to this case. The mean free path of the $^3\Pi^+$ iodine molecules was thus determined to be $\sqrt{D\tau} = (3 \pm 2) \times 10^{-6}$ cm. It was concluded that no significant energy transfer between iodine molecules takes place and the photoinjection reaction can be described by

$$I_2^* + 2M \to 2M^+ + 2I^-$$
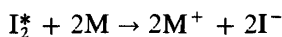
# REFERENCES

[1] W. Mehl and J. M. Hale. "Insulator Electrode Reactions", in *Advances in Electrochemistry and Electrochemical Engineering* (Ed. P. Delahay and C. W. Tobias) Vol. 6, pp. 399–458. Interscience, New York (1967) and other references quoted there.

[2] N. F. Mott and R. W. Gurney. *Electronic Processes in Ionic Crystals*, p. 170. Oxford University Press: London (1940).

[3] K. Klier. *Coll. Czech. Chem. Commun.* **27**, 920 (1962).

[4] F. Lohmann. *Surface Science* **14**, 431 (1969).

[5] R. H. Fowler. *Statistical Mechanics*, p. 364. Cambridge University Press: London (1966).

[6] W. Mehl, J. M. Hale and M. H. Davies. Publication being prepared.

[7] O. H. Le Blanc. *J. Chem. Phys.* **35**, 1275 (1961).

[8] N. S. Hush. Unpublished manuscript.

[9] P. Balk, S. de Bruijn and G. J. Hoijtink. *Mol. Phys.* **1**, 151 (1958) and further references quoted there.

[10] R. S. Becker and E. Chen. *J. Chem. Phys.* **45**, 2403 (1966).

[11] B. Case, N. S. Hush, R. Parsons and M. E. Peover. *J. Electroanal. Chem.* **10**, 360 (1965).

[12] W. E. Wentworth and R. S. Becker. *J. Am. Chem. Soc.* **85**, 2210 (1963).

[13] N. S. Hush and J. A. Pople. *Trans. Faraday Soc.* **51**, 600 (1955).

[14] F. Lohmann and W. Mehl. *Ber. Bunsenges. Physik. Chem.* **77**, 493 (1967).

[15] M. A. Lampert and P. Mark. *Current Injection in Solids* Academic Press: New York (1970).

[16] N. S. Hush. *Trans. Faraday Soc.* **57**, 557 (1961).

[17] R. A. Marcus. *Ann. Rev. Phys. Chem.* **15**, 155 (1964).

[18] R. R. Dogonadze, A. M. Kuznetsow and Yu. A. Chizmadzhev, *Russ. J. Phys. Chem.* (English Transl.) **38**, 652 (1964).

[19] R. R. Dogonadze and Yu. A. Chizmadzhev. *Proc. Acad. Sci. USSR, Phys. Chem. Sect.* (English Transl.) **150**, 402 (1963).

[20] W. Aalbersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland. *J. Chem. Soc.* **3055** (1959).

[21] A. K. Hoffmann. *Nature* **218**, 1157 (1968).

[22] N. Geacintov and M. Pope. *J. Chem. Phys.* **45**, 3884 (1966).

[23] *Landolt–Börnstein* (Ed. K. H. and A. M. Hellwege) Vol. II, Sect. 6, p. 913. Springer: Berlin (1959).

[24] W. A. Holmes-Walker and A. R. Ubbelohde. *J. Chem. Soc.* 720 (1954).

[25] F. Lohmann and W. Mehl. *J. Chem. Phys.* **50**, 500 (1969).

[26] H. G. Smith and R. E. Rundle. *J. Am. Chem. Soc.* **80**, 5075 (1958).

[27] I. Gränacher. *Solid State Commun.* **2**, 365 (1964).

[28] J. L. Garnett and R. J. Hedges. *Chem. Commun.* 1220 (1967).

[29] J. T. Davies and E. K. Rideal. *Interfacial Phenomena*, pp. 184/185. Academic Press: New York (1963).

[30] H. Kallmann and M. Pope. *J. Chem. Phys.* **32**, 300 (1960).

[31] J. M. Hale and W. Mehl. *Electrochim. Acta* **13**, 1483 (1968).

[32] W. Mehl and J. M. Hale. *Discussions Faraday Soc.* **45**, 30 (1968).

[33] W. Mehl and J. M. Hale. *Ber. Bunsenges. Physik. Chem.* in print.

[34] Th. Förster. *Ann. Physik* **2**, 55 (1947).

[35] W. Mehl and B. Funk. *Physics Letters* **25A**, 364 (1967).

[36] J. Dresner. *Phys. Rev.* **143**, 558 (1966).

[37] R. Williams and J. Dresner. *J. Chem. Phys.* **46**, 2133 (1967).

[38] L. Brewer, R. A. Berg, and G. M. Rosenblatt. *J. Chem. Phys.* **38**, 1381 (1963).

[39] W. Mehl, J. M. Hale and J. S. Drury. *Ber. Bunsenges. Physik. Chem.* **73**, 855 (1969).

[40] L. E. Lyons and J. C. Mackie. *Proc. Chem. Soc.* (London) **71**, (1962).

[41] W. Mehl. *Solid State Comm.* **6**, 549 (1968).

[42] A. Many, J. Levinson and I. Teucher. *Mol. Cryst.* **5**, 121 (1968).