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The Temperature Dependence of Hole Injection into Anthracene Crystals

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The temperature dependence of dark- and photo-currents was studied for the hole injection into anthracene crystals between 0 and 30°C. It was observed that the photocurrent or, as has been previously established, the electron-transfer rate from an excited anthracene crystal to an acceptor had a small temperature dependence, while the dark current or the electron-transfer rate from the crystal in its ground state to an acceptor had a definite value of activation energy. The observed small activation entropy for the dark reaction was interpreted in terms of Marcus' theory, and the small polarizability of the organic crystal was, accordingly, suggested to increase the probability of the electron transfer.

During the past few years, a considerable number of studies have been concerned with the electron-transfer reactions involving organic molecules. The hole injection into an organic crystal from electrodes is regarded as a reaction of this type. The saturation current which appears in a sufficiently high voltage region is associated with the rate of the electron-transfer process between the organic molecule (Ar) on the crystal surface and an organic or inorganic acceptor (M) in an electrode;

$$\mathrm{Ar} + \mathrm{M} \longrightarrow \mathrm{Ar}^+ + \mathrm{M}^- \qquad (1)$$

Although some pieces of evidence indicate that a qualitative interpretation of this reaction is possible on the basis of the "outersphere" type of reaction mechanism, no direct measurement has yet been performed to show that this process has an activation free energy such as is predicted by the theory.

This work is concerned with the temperature dependence of the saturation current and, for the most part, deals qualitatively with the factors influencing the rate of this process.[*2]

Several previous theoretical discussions have been presented, notably by Mehr.1) Applying Marcus' theory,2) he attempted to calculate the probability of the electron transfer from an organic crystal to an electron acceptor. His results demonstrated a qualitative agreement with the experimental results. It is, however, still open to question whether or not the theory is consistent with the temperature dependence and other features of the process.

In the present work, an attempt has been made to estimate the activation free energy and to examine the applicability of the Marcus theory.

Experimental

Single crystal platelets of zone-refined anthracene about 50 μ-thick were obtained by the sublimation technique. They were mounted with paraffin wax on the glass cell which is shown in Fig. 1. The back side of the cell, on which the negative potential was applied, contained an aqueous solution of the injecting species. The surface area of the anthracene crystal in contact with the solution was about 0.01 cm^2.

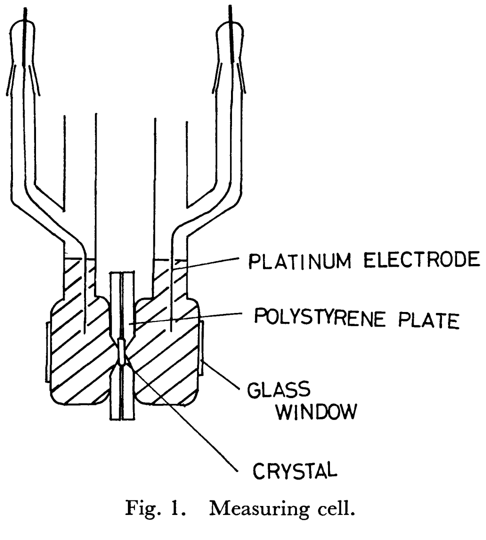

Fig. 1. Measuring cell.

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[*2] Recently Sworakowski reported the temperature dependence of the hole injection into anthracene crystals from an electrode containing inorganic oxidants. J. Sworakowski, *Acta Phys. Pol.*, **35**, 33 (1969).

1) W. Mehl and T. M. Hale, *Discuss. Faraday Soc.*, **45**, 30 (1968).

2) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); **38**, 1858 (1963).

When the dc photocurrent in the above arrangement was measured, the front side was illuminated by a tungsten lamp with a filter which had a maximum transmission at 401 nm and a half width of 11 nm.

The current was measured with a Kawaguchi-type, direct coupled ammeter, Model NA-12E.

The crystals of the other organic molecules were obtained in the following ways:

a) Tetracene was purified by repeated sublimation and was sublimed in a sealed tube under N_2 atmosphere to form single crystals.

b) Phenanthrene and *p*-terphenyl were zone-refined, and single crystals of them were obtained by the sublimation method.

The temperature of the cell was controlled by immersing it in a thermostated water bath.

Results

A. Photocurrents. Ethanol acted as a hole-injecting electrode for the illuminated anthracene crystal, and the various electron acceptors in the electrode were shown to enhance the hole-photocurrent.[3] Phthalonitrile (PN) dissolved in the ethanol electrode was found to enhance the photocurrent, as is shown in Fig. 2. It had previously been observed that tetrachlorophthalonitrile (TCPN) had a similar, but stronger, effect.[3] The increase in the current was proportional to the concentration of the acceptor in both cases. No absorption of light in this wavelength region was found by PN or TCPN. Therefore, the increase in the current is due to the reaction:

$$Ar^* + PN(\text{or TCPN}) \longrightarrow Ar^+ + PN^-(\text{or TCPN}^-)$$

where Ar^* is an electronically-excited anthracene and where Ar^+ is an anthracene cation.

The temperature dependence of the photocurrents for the anthracene crystal with the ethanol electrode containing PN or TCPN was measured. The results are shown in Fig. 3 and Table 1. Table 1 gives the apparent activation energy and the magnitude of the saturation currents at room temperature. The difference in the apparent activation energy between PN and TCPN determined experimentally is 1.8 kcal/mol. On the other hand, from the value of the saturation current at room temperature, PN is calculated to have an activation energy about 2.1 kcal/mol larger than TCPN, assuming that they have the same activation entropy.

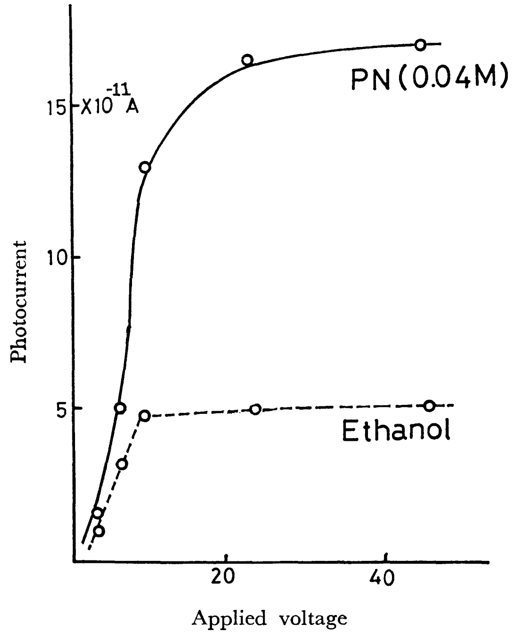

Fig. 2. Voltage dependence of photocurrents in anthracene crystal.
Electrode arrangement: Water|Anthracene| Ethanol or Phthalonitrile in Ethanol

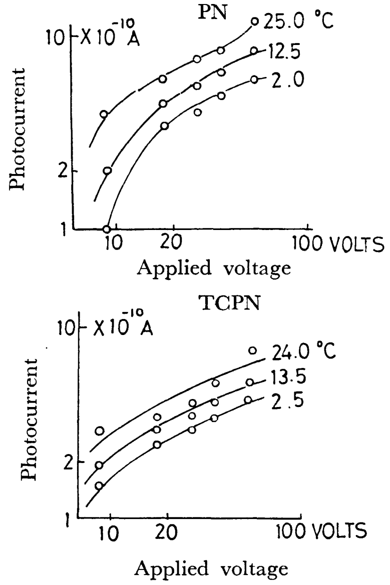

Fig. 3. Temperature dependence of photocurrents in anthracene crystal.
Electrode arrangement: Water|Anthracene| Phthalonitrile or Tetrachlorophthalonitrile in Ethanol

TABLE 1. THE TEMPERATURE DEPENDENCE OF THE SATURATION PHOTO-CURRENT DUE TO THE HOLE INJECTION FROM THE ETHANOL ELECTRODE CONTAINING ORGANIC ELECTRON ACCEPTORS

Electrode	Saturation current at room temperature Amp/cm^2	Apparent activation energy, kcal/mol
Ethanol	4×10^{-11}	0.5
TCPN(10^{-3}M)	2600	2.3
PN(10^{-3}M)	70	4.1

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[3] M. Soma, *J. Amer. Chem. Soc.*, **92**, 3289 (1970).

B. Dark Current. Most of the dark-injecting ions corroded the crystal surface because of their strong oxidizing power. Accordingly, the dark currents more or less decreased with the time.

$K_2Cr_2O_7$ in aqueous H_2SO_4 provided a rather stable dark current, which was kept constant for almost two hours. The results of the temperature dependence measurements of the saturation dark current for the electrode containing $K_2Cr_2O_7$ are shown in Table 2. It definitely confirms that the dark current has a constant activation energy over the measured temperature range, which was not necessarily the case for the photocurrent. An additional experiment, which examined the dependence of the saturation dark current on the concentration of $K_2Cr_2O_7$ and the proton, indicated that the saturation dark current follows the expression $i_d = k[HCrO_4^-][H^+]^2$, where k is a constant value and where $[HCrO_4^-]$ and $[H^+]$ are the concentrations of the $HCrO_4^-$ ion and the proton respectively.

Table 2. The temperature dependence of the saturation current due to the hole injection by $K_2Cr_2O_7$ (3×10^{-3}M in 1.1NH_2SO_4) into anthracene crystal

Temperature, °C	Saturation current Amp/cm²	Apparent activation energy, kcal/mol
0.5	1.2×10^{-7}	11
12.2	2.4	11
22.0	4.7	12
33.0	9.4	—

In addition, when sulfuric acid was replaced by deuterated sulfuric acid, and the solvent, by heavy water, the current was found to increase by a factor of 3.3 or the kinetic isotope effect was $i_H/i_D = 1/3.3$. These facts suggest that protons are involved in this electron-transfer reaction.

In the case of an aqueous solution of the Ce^{4+} ion, the dark current decreased rather rapidly with the time. The reproducible initial values, however, were obtained by washing the crystal surface with ethanol. The temperature dependence was obtained by this technique; the results are given in Fig. 4.

Since the current was proportional to the concentration of the Ce^{4+} ion and was almost independent of the concentration of H_2SO_4 in the range of 0.1—1.0M, it may be concluded that a one-step electron-transfer reaction takes place from the molecule at the crystal surface to the Ce^{4+} ion or, specifically, the $Ce(SO_4)_3^{2-}$ complex ion.[4)]

Taking the collision frequency as 2×10^{24} cm^{-2} sec^{-1}mol^{-1}, the activation entropy and free energy were calculated to be as shown in Table 3, in which the thermodynamic data for the isotopic exchange reaction of cerium ions[5)] are given for comparison. It is demonstrasted that the activation entropy for the present reaction is considerably smaller than that for the homogeneous reaction. This feature will be discussed in the following section in terms of the Marcus theory.

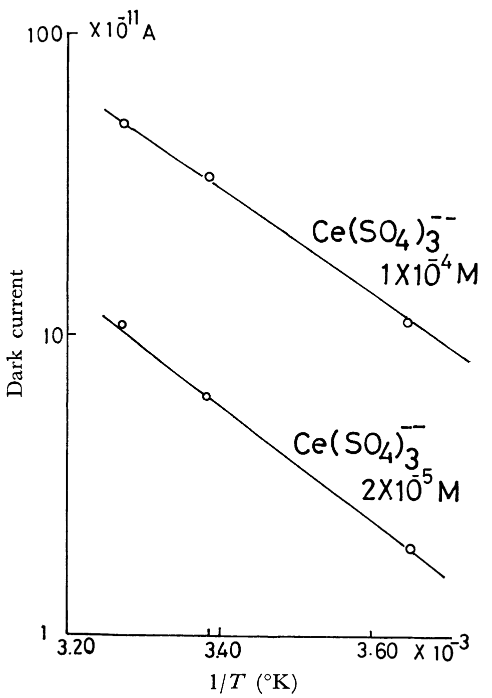

Fig. 4. Temperature dependence of dark currents in anthracene crystal.
Electrode arrangement: Water|Anthracene| Ce^{4+} in aqueous H_2SO_4

The dark currents due to the hole injection by Ce^{4+} into various organic crystals were measured at room temperature. As is shown in Fig. 5, all the crystals exhibited current-voltage characteristics similar to those of anthracene. In Table 4, the saturation currents and the activation free

Table 3. Thermodynamic parameters for the electron transfer reaction in the system $Ce(SO_4)_3^{2-}$/anthracene crystal and Ce^{4+}/Ce^{3+} in aqueous solution[5)]

System	Activation enthalpy kcal/mol	Activation entropy e.u.	Activation free energy kcal/mol
$Ce(SO_4)_3^{2-}$/ Anthracene	8.7	−3.5	10.7
Ce^{4+}/Ce^{3+}	7.7	−40	19.3

[4)] T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

[5)] J. W. Gryder and R. W. Dodson, *J. Amer. Chem. Soc.*, **73**, 2890 (1951).

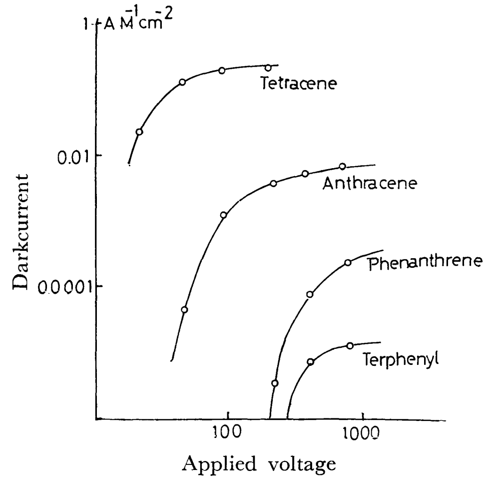

Fig. 5. Voltage dependence of dark currents in various organic crystals.
Electrode arrangement: Water|Crystal|Ce^{4+} in aqueous H_2SO_4

TABLE 4. HOLE INJECTION INTO ORGANIC CRYSTALS FROM CERIC ELECTRODE

Crystal (ionization energy, eV)	Saturation dark current Amp/cm^{2}M	$\Delta F^{\ddagger}$ (obs.) kcal/mol	ΔF° kcal/mol	$\Delta F^{\ddagger}$ (calcd)[a] kcal/mol
Tetracene (5.32)	13000×10^{-5}	9.0	−16.8	7.5
Anthracene (5.65)	7500	10.7	−9.2	10.7
Phenanthrene (6.45)	250	12.8	6.9	20.8
Terphenyl[b] (6.71)	11	14.6	15.2	23.8

a) Calculated by assuming λ is 59 kcal/mol
b) Estimated from the charge transfer band of the tetracyanoethylene complex in CH_2Cl_2,[6] setting the polarization energy equal to that of naphthalene crystal.[7]

energies are given; the latter were calculated by assuming that the activation entropy is equal to that for anthracene.

Discussion

A. Activation Free Energy. By applying the Marcus theory to the present system, the free energy of activation for the electron-transfer reaction (1) at the surface of organic crystals is expressed as follows:

$$\Delta F^{\ddagger}=\frac{\lambda}{4}\left(1+\frac{\Delta F^0}{\lambda}\right)^2 \tag{2}$$

where ΔF° denotes the standard free energy change in the reaction (1) and λ is the energy parameter relating to the orientation of solvent molecules in an activated state. When the reactants are approximated by charged conducting spheres, λ is expressed as:

$$\begin{aligned}\lambda=&\frac{1}{2a_1}\left(\frac{1}{D_{\mathrm{op}_1}}-\frac{1}{D_{\mathrm{s}_1}}\right)+\frac{1}{2a_2}\left(\frac{1}{D_{\mathrm{op}_2}}-\frac{1}{D_{\mathrm{s}_2}}\right)\\&-\frac{2}{r_1+r_2}\left(\frac{1}{D_{\mathrm{op}_1}+D_{\mathrm{op}_2}}-\frac{1}{D_{\mathrm{s}_1}+D_{\mathrm{s}_2}}\right)\\&+\frac{1}{4r_1}\left\{\frac{D_{\mathrm{op}_1}-D_{\mathrm{op}_2}}{D_{\mathrm{op}_1}(D_{\mathrm{op}_1}+D_{\mathrm{op}_2})}-\frac{D_{\mathrm{s}_1}-D_{\mathrm{s}_2}}{D_{\mathrm{s}_1}(D_{\mathrm{s}_1}+D_{\mathrm{s}_2})}\right\}\\&+\frac{1}{4r_2}\left\{\frac{D_{\mathrm{op}_2}-D_{\mathrm{op}_1}}{D_{\mathrm{op}_2}(D_{\mathrm{op}_1}+D_{\mathrm{op}_2})}-\frac{D_{\mathrm{s}_2}-D_{\mathrm{s}_1}}{D_{\mathrm{s}_2}(D_{\mathrm{s}_1}+D_{\mathrm{s}_2})}\right\}\end{aligned} \tag{3}$$

where the 1 and 2 indices refer to the crystal and the electrode medium respectively; where D_{OP} and D_{s} are the optical and static dielectric constants; r ,the distance between the center of a change and the boundary of the two phases, and a, the radius of a charged sphere. The last two terms in (3) arise from the interaction between a real charge and an image charge induced in each medium. It is evident that Eq. (3) gives the known formula for the electron-transfer reaction in the homogeneous phase when $D_1=D_2$, and for the electrochemical case at metal electrodes when D_1 is infinite.

B. Photocurrent. In a previous paper,[3] it was concluded that the electron-transfer reaction from an excited anthracene at the surface of the crystal to TCPN is almost diffusion-controlled. The present low value of the activation energy for TCPN confirms this; it may be attributed to the diffusion process. The relatively large activation energy for PN may arise from the lower electron affinity. Table 5 gives a rough estimation of ΔF°, the free-energy change of the reaction for each acceptor. It shows that a change of about 0.5 eV in ΔF° caused a change of about 0.09 eV (Table 1) in the activation free energy. As this difference

TABLE 5. THE ESTIMATION OF THE FREE ENERGY CHANGE ΔF° FOR THE PHOTO HOLE INJECTION

Acceptor	Electron affinity (eV)	Solvation energy (eV)	ΔF°[a] (eV)
PN	1.1[b]	2.2[c]	−0.7
TCPN	1.6[d]	2.2[e]	−1.2

a) ΔF°=(ionization energy of anthracene crystal, 5.7 eV) −(electron affinity of acceptor+solvation energy+photon energy, 3.1 eV).
b) Ref. 8.
c) Calculated from the difference between the reduction potential in polar organic solvent and the gaseous electron affinity.[8]
d) Estimated from the charge transfer band of pyrene-complex in $CHCl_3$.
e) Assumed to be the same with PN.

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[6] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).

may be attributed to the difference in $\Delta F^{\ne}$ expressed by Eq. (2), the required value of λ is about 1.4 eV. On the other hand, the theoretical estimate gives λ to be about 0.5 eV using Eq. (3), where the radius, a, for the acceptor is assumed to be 3.3 Å and that for anthracene to be 3.0 Å, those values being consistent with the experimental solvation energy in polar solvents[8] and with the polarization energy in the crystal[7] respectively. The experimental value of λ is considerably larger than the theoretical one. As the electron-transfer reaction can reasonably be described as an "outer-sphere" type,[9] this discrepancy cannot be attributed to the contribution of the reorganization in "inner-sphere" to λ, but must be attributed to some flaws in estimating ΔF° and λ, or in the theory itself.

C. Dark Current. According to the Marcus theory, the greater part of the free energy of activation in the electron-transfer process is to be attributed to the reorientation of solvent molecules in the activated state, in which they are not electrostatically in equilibrium. This brings about a largely negative activation entropy, since the solvent molecules lose many degrees of freedom in such a state.

The present system is considered to have half of its medium replaced by an anthracene crystal. Since anthracene crystals have a negligible orientational polarizability as compared with water, the observed low value of the activation entropy supports this prediction.

In order to put this interpretation into more quantitative form, we will below calculate for various cases, since λ determines the main part of the free energy of activation and, moreover, includes the contribution of the solvent molecules described above in terms of polarizability. The λ's were calculated in three cases: 1. the present system (Ce^{4+}/anthracene crystal), 2. the electron-transfer reaction from an anthracene molecule to Ce^{4+} in a water solvent, 3. the homogeneous reaction between Ce^{4+} and Ce^{3+}. The resulting λ's were 0.35 eV, 1.35 eV, and 0.66 eV respectively. These values are calculated from Eqs. (2) and (3), assuming that a_1 of an anthracene molecule is 3.5 Å, and the a_2 values of Ce^{4+} and Ce^{3+} ions, 6 Å. The assumed value of a_1 is obtained as the mean value of the required radius for the ion in polar solvents and in the crystal, while that of a_2 is obtained as a sum of the bond lengths and the van der Waals radius of an oxygen ion. The above results show that value for the (1) reaction is the smallest, or the presence of anthracene crystals lowers the $\Delta F^{\ne}$ because of its low polarizability; this finding is in qualitative agreement with the experimental observations shown in Table 3.

The results given in Table 4 show that the saturation current or electron-transfer rate increases as the ionization potential decreases. It should, however, be noted that the change in the activation free energy with the ionization energy is much smaller than that predicted by Eq. (2). In making this discrepancy clear, we calculated the activation free energy from Eq. (2), assuming each crystal have the same value λ (59 kcal/mol) as anthracene.

Mehr noticed[10] that, in the case of naphthalene crystals, the dark current for Ce^{4+} is much larger than predicted by Eq. (2). He attributed this to the formation of a charge-transfer complex between the naphthalene molecule and the Ce^{4+} ion. However, the present results suggest that the small dependence of the current on the ionization potential is not limited to naphthalene but is, rather, common to all crystals. This fact makes us doubt the applicability of Eq. (2). The real situation may be that, although λ determines the greater part of the activation free energy, $\Delta F^{\ne}$ dose not depend on λ and ΔF° in the way expressed by Eq. (2).

The authors are grateful to Professor Kenzi Tamaru for his constant encouragement and helpful discussions throughout this work.

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7) L. E. Lyons and G. C. Morris, *J. Chem. Soc.*, **1960**, 5192.

8) A. L. Farragher and F. M. Page, *Trans. Faraday Soc.*, **63**, 2369 (1967).

9) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).

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