

Photoinduced Electron-Transfer Reactions at the Surface of Organic Crystals

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Abstract: Photoinduced electron-transfer reactions between single crystals of aromatic hydrocarbons and organic electron acceptors were investigated by measuring the photoconductivity of crystals. The reaction involves excited hydrocarbons or electron acceptors and shows high quantum efficiency. In some cases the reaction takes place *via* formation of charge-transfer-type complexes at the surface.

The electron-transfer phenomena at the interface between organic crystals and another phase, which may be gaseous, liquid, or solid, containing electron-donor or -acceptor molecules, have been the subject of considerable reports.¹ Among them the photoinduced electron-transfer processes are interesting not only from the physico-chemical viewpoint about the reactivity of excited molecules but also from the biological view point because of their possible correlation to the primary processes of the photosynthesis in the photosynthetic tissues.² Concerning the problem two important experiments were carried out; one was reported by Kearns, Tollin, and Calvin³ and the other by Kallmann and Pope.⁴ Calvin and his coworkers examined the effects of added electron acceptors such as quinones on the dark conductivity as well as the photoconductivity of the sublimed film of phthalocyanine, which was considered to be the model system for the chlorophyll-plastoquinone system in the photosynthetic apparatus. Kallmann and Pope studied photoconductivity of the anthracene single crystal in a sandwich-type electrode arrangement, using an electrolyte solution as an electrode. Very efficient photoinduced hole injection into the anthracene crystal from the electrode was observed, caused by the electron transfer from anthracene to the solution.

In this report photoinduced electron-transfer reactions between single crystals of aromatic hydrocarbons and organic molecules in the electrode were investigated using Kallmann- and Pope-type arrangements of electrodes.

If the current in the molecular crystal is attributed to the carrier injection from the electrode, the magnitude of the current is limited by the rate of carrier injection from the electrode. Accordingly, we can find the rates of electron-transfer reactions at the electrode from measurement of the saturation current, by applying sufficiently high voltages.⁵

Experimental Section

Preparation of Single Crystals. The thin plates of single crystals desired for the measurements were prepared as follows using com-

mercial aromatic hydrocarbons as starting materials. *p*-Terphenyl was recrystallized repeatedly from a xylene solution, and thin flaky crystals of *p*-terphenyl were also grown in a xylene solution. Single crystals of anthracene were obtained from solution by Kallmann and Pope's method⁵ after purification by repeated recrystallization and sublimation *in vacuo*. Another method was sublimation of anthracene powder sealed in a glass tube with nitrogen gas by heating it in an electric furnace. Single crystals grew on the cooled part of the glass wall. Sometimes a zone-refining technique was applied after the prepurification described above. Zone-refined anthracene was used only for the crystal growth by sublimation. The purity of the crystal greatly affected the current-voltage characteristic, but had little effect on the saturation levels of the current. Zone refining was not always necessary for our purpose. Pyrene and perylene were purified by repeated chromatographic separation on an alumina column and sublimation *in vacuo*. Single crystals of pyrene were obtained from a xylene solution by slow evaporation of the solvent. Crystals of perylene were grown by sublimation in a sealed tube. Tetracene was purified by repeated sublimation *in vacuo* more than four times. The technique for growing crystals was similar to that for anthracene or perylene.

Measuring Cell. A cell suitable to measure the photoconductivity of thin organic crystals was first designed by Kallmann and Pope.⁶ Our cell shown in Figure 1 is a modified type which could be built more easily.

A rectangular parallelepiped of dimensions 25 × 25 × 15 mm was cut out from a polystyrene plate 15 mm thick. The entire cell consisted of two symmetric half cells. A crystal was fixed with vacuum grease between the half cells, each of which had a hole in the center of the square plane. The whole hollow bounded by the crystal and the window was the container of the liquid used as electrode material.

Experimental Procedures. Contact between the liquid electrode and the measuring system was made by platinum wires. The applied voltage was supplied by dc dry batteries. Current was measured by a Kawaguchi dc-amplifier-type nanoammeter or a Kawaguchi vibrating reed electrometer.

For photoconductivity measurements, two light sources were employed. The crystals were illuminated by a 100-W tungsten lamp for excitation by white or panchromatic light. For excitation by monochromatic light metal interference filters were used with a 750-W tungsten lamp. Thus monochromatic light of wavelengths longer than 4000 Å was obtained at intervals of 500 Å. The half width of the light transmitted through the filters ranged from 110 to 160 Å. The intensity of the incident light, which was varied by controlling the ac voltage applied to the tungsten filament, was determined by simultaneous use of a thermopile and a germanium phototransistor.

Results

The illustrative example is the system in which tetrachlorophthalonitrile (TCPN) is used as an electron acceptor. As TCPN has no absorption bands located in the range longer than 3400 Å, the excitation of an anthracene crystal by light of wavelength longer than 4010 Å is not affected by its presence; therefore, its addition

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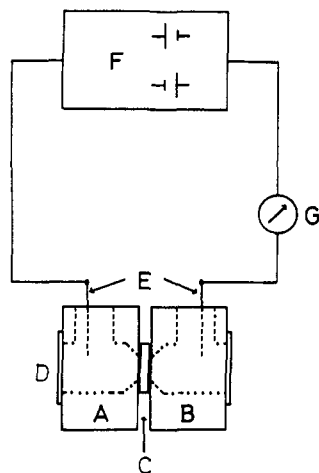


Figure 1. Measuring cell: A and B, polystyrene half cells; C, crystal; D, window; E, platinum wires; F, voltage supply.

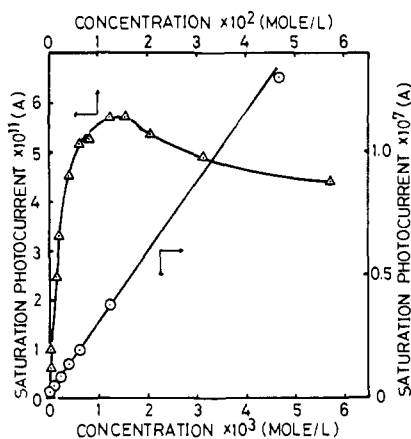


Figure 2. Variation of the saturation photocurrent in an anthracene crystal with concentration of added electron acceptors: \odot , I_{ps}^+ for the anthracene-TCPN system excited by 4010-Å light; electrode arrangement, ethanol + TCPN|anthracene|water; electrode area, 3×10^{-2} cm²; Δ , I_{ps}^- for the anthracene-*p*-benzoquinone system excited by white light; electrode arrangement, water|anthracene|ethanol + *p*-benzoquinone; electrode area, 0.1 cm².

to the illuminated electrode is appropriate. In Figure 2 the saturation photocurrents for the positive electrode illumination, I_{ps}^+ (through the following sections, I_p^+ denotes the photocurrent when the illuminated electrode is positive, I_p^- the photocurrent when the illuminated electrode is negative, and I_{ps} the saturation photocurrent), by light of 4010 Å are plotted against the concentration of TCPN, showing the linear dependence of the increase in photocurrents on the concentration of TCPN. This linear concentration dependence held at least up to 0.00468 mol l.⁻¹, the concentration which corresponds to the saturated solution of TCPN.

As is shown in Figure 3, the saturation photocurrent for the TCPN electrode is proportional to the intensity of incident light as is the case for the water electrode. The spectral dependence of the normalized photocurrents was also the same, in the wavelengths region investigated, as that when the water electrode was used.

The linear relationship between photoinduced hole currents and the concentration of the added acceptor also holds in the *p*-terphenyl-*o*-chloranil system. The range of the concentrations investigated was much wider than in the anthracene-TCPN system.

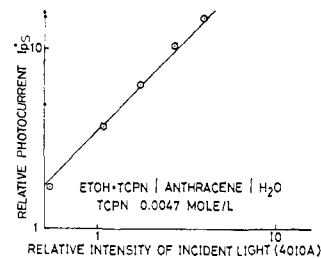


Figure 3. Changes in the saturation photocurrent in the anthracene-TCPN system with intensity of incident light; electrode area, 3×10^{-2} cm²; maximum photo flux, 3×10^{14} photons cm⁻² sec⁻¹.

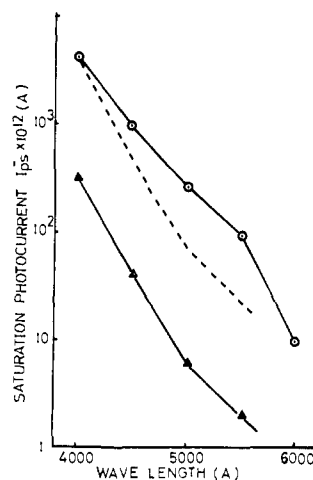


Figure 4. Changes in the spectral response of the saturation photocurrent (I_{ps}^-) in an anthracene crystal with addition of *o*-chloranil: Δ , without *o*-chloranil; \odot , with *o*-chloranil; the dotted line is parallel to the lower line. Photocurrents were not normalized for equal light intensity.

o-Chloranil is a good electron acceptor for anthracene as well. The spectral dependence of the saturation photocurrent for the ethanol electrode with and without *o*-chloranil is shown in Figure 4. While 4010-Å light mostly excites the anthracene molecule, light of longer wavelength does not excite anthracene but excites *o*-chloranil molecules.

The effect of added *o*-chloranil on the electrical conductivity of the various aromatic hydrocarbon crystals is summarized in Table I.

Another typical example of concentration dependence is the anthracene-*p*-benzoquinone system. Figure 2 shows changes in the saturation photocurrents as a function of the concentration of *p*-benzoquinone dissolved in the electrode. In the low-concentration range the photocurrent increases as the concentration of *p*-benzoquinone increases, but it tends to saturate as the concentration becomes larger, reaches a maximum, and begins to decrease slowly with the further addition of the acceptor molecules. When $C/\Delta I_{ps}^-$, where ΔI_{ps}^- is the increase in the saturation photocurrent with the addition of the acceptor to the electrode, is plotted against the concentration, C , of *p*-benzoquinone, up to the concentration (C_m) at maximum increase in the photocurrent, a linear relationship is found as is illustrated in Figure 5.

A similar concentration dependence of the photocurrent was found for the *p*-terphenyl-*p*-benzoquinone system. In this case saturation of the photocurrent was

Table I. Effects of Added *o*-Chloranil on Dark Currents and Photocurrents in Some Hydrocarbon Crystals^a

Hydrocarbon (electrode area, cm ²)	Crystal thickness, μ	Applied voltage, V	Concentration of <i>o</i> - chloranil, mol l. ⁻¹	Dark current, $I_d \times 10^{12}$ A	Photocurrent, $I_p^- \times 10^{12}$ A
<i>p</i> -Terphenyl (0.3)	84	90	0	0.6	1.1
			0.13	1.4	1700
Anthracene (0.3)	120	90	0	0.6	17.4
			0.10	4.9	5450
Tetracene (0.009)	30	45	0	2.8	71.2
			0.10	100	214
Perylene (0.03)	80	550	0	7.5	270
			0.10	100	5500
Pyrene (0.009)	350	180	0	0.6	0.7
			0.10	2.0	110

^a Electrode arrangement, water|crystal|ethanol + *o*-chloranil (*o*-chloranil was dissolved in the dark-side electrode).

attained by increasing the acceptor concentration, but the photocurrent did not fall again in the concentration range of the observed decrease in the anthracene-*p*-benzoquinone system.

The electron-transfer reactions between the crystals and electron donors in the electrode can be examined by a method similar to that described above. The photocurrents, I_p^- , for illumination of the negative electrode, were measured using an ethanol electrode in both sides with or without *p*-phenylenediamine in the electrode. The results are shown in Table II.

Table II. Effects of Added *p*-Phenylenediamine on Photocurrents in the Anthracene Crystal^a

Applied voltage, V	Photocurrent, ^b $I_p^- \times 10^{12}$ A	
	Without <i>p</i> - phenylenediamine	With <i>p</i> -phenylene- diamine ^c
1.5	0.9	3.1
4.5	1.5	9.2
9	2.1	21.8
22.5	3.3	37.8
45	5.3	88.7
90	9.2	157

^a Electrode arrangement, ethanol + *p*-phenylenediamine|anthracene|ethanol. Crystal thickness 40 μ , electrode area ~ 0.1 cm².
^b The crystal was illuminated by a 100-W tungsten lamp. ^c Concentration 3.7×10^{-2} mol/l.

Discussion

The increase in the saturation photocurrent with the addition of electron acceptors to the electrode is attributed to photoinduced electron transfer from anthracene to acceptor molecules, resulting in hole injection into the crystal. The magnitude of the saturation currents is important because it is directly correlated with the rate of electron transfer at the interface. Knowing the saturation current proportional to the number of electrons which cross the interface of the crystal and the electrode, the rate of electron-transfer reactions can be calculated easily.

The linear dependence of the sensitized photocurrent on the concentration of added TCPN strongly supports the argument that by measuring the saturated photocurrents, we really observed the electron transfer process at the crystal surface. The photocurrent for the electrode containing a saturated ethanol solution of TCPN was much larger than that for the water electrode. The former was 1.3×10^{-7} and the latter 3.5×10^{-8} A. The corresponding quantum efficiency was about 0.1 for hole injection into anthracene from the

saturated ethanol solution of TCPN. As the concentration of TCPN is only limited by its solubility in ethanol, and the linear relationship between the concentration and the number of holes injected per unit time still holds for a saturated solution of TCPN, the quantum efficiency might be made to become unity by the use of more concentrated solution as electrodes and by illumination by more strongly absorbed light.

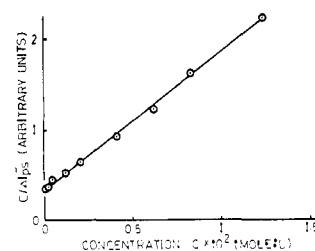
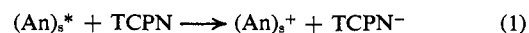


Figure 5. Langmuir-type plot for the increase in the saturation photocurrent in the anthracene-*p*-benzoquinone system.

Changes in the sensitized photocurrent with incident light intensity and wavelength suggest the following one-photon reaction scheme for the electron transfer at the surface



where $(\text{An})_s^*$, an excited anthracene molecule at the surface, is produced by direct photon absorption at the surface anthracene array or by exciton migration from the interior of the crystal to the surface.

The reaction cross section σ_R for the anthracene-TCPN system excited by 4010-Å light can be estimated roughly by the equation

$$\sigma_R = \sigma Q_E \frac{1}{\tau N_c}$$

where σ is the geometrical cross section of an anthracene molecule in the surface of the crystal (*ab* plane), Q_E is the reaction yield per exciton reached at the surface, τ is the exciton lifetime at the surface, and N_c is the number of collisions between TCPN and an anthracene molecule per unit time. τ is unknown, so the exciton lifetime in the bulk crystal was used instead. Substituting the numerical values $\sigma = 26 \text{ \AA}^2$, $Q_E = 0.3$, $N_c = 2 \times 10^7 \text{ sec}^{-1}$, $\tau = 2 \times 10^{-8} \text{ sec}$, σ_R is roughly equal to σ . Accordingly it was concluded that the reaction was almost diffusion limited.

In the case of the *p*-terphenyl-*o*-chloranil system the photoinduced electron-transfer reaction was considered to occur between the excited acceptor molecule and a *p*-terphenyl molecule at the surface as follows $p\text{-terphenyl} + o\text{-chloranil}^* \longrightarrow p\text{-terphenyl}^+ + o\text{-chloranil}^-$ (2) because no absorption bands for *p*-terphenyl were observed in the examined spectral region. Actually rough similarity between the action spectra for the photoinduced hole injection and the absorption spectra of *o*-chloranil solution was observed.

For the anthracene-*o*-chloranil system the observed spectral dependence suggests that two mechanisms of types 1 and 2 occurred, where type 1 is the electron-transfer reaction between an excited donor molecule and a normal acceptor molecule and type 2 is the electron transfer between a normal donor and an excited acceptor.

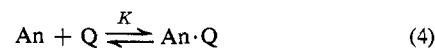
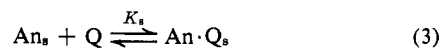
In comparing the effect of *o*-chloranil on the photocurrents of the various hydrocarbons it should be taken into consideration that the generation of charge carriers in the bulk of the crystal could not be neglected in the tetracene⁷ and the perylene crystals. The dark conductivity of the perylene and tetracene crystals, which have relatively lower ionization potentials, was markedly enhanced by the presence of *o*-chloranil molecules. This means that in these cases even without illumination the electron transfer between the crystals and *o*-chloranil occurred to some extent, which is similar to the result for the effect of *o*-chloranil on the dark conductivity of sublimated films of these hydrocarbons.⁸ The hole injection in the dark could not be observed when the ethanol solution of *p*-benzoquinone, whose electron affinity is smaller than that of *o*-chloranil, was used. Generally the electron acceptors which have electron affinities comparable to or larger than that of *p*-benzoquinone enhanced the photoconductivity of the aromatic hydrocarbons in Table I.

The concentration dependence of the enhanced photocurrent in anthracene with added *p*-quinone is analogous to a Langmuir plot for the adsorption isotherm (Figure 5), demonstrating that the electron transfer induced by illumination occurs between anthracene molecules at the surface of the crystal and the adsorbed layer of *p*-benzoquinone molecules. At C_m , a monomolecular layer of *p*-quinone was formed and further deposition of the *p*-benzoquinone on this monomolecular layer reduced somewhat the overall rate of electron transfer between the crystal and the electrode.

The magnitude of C_m in the *p*-terphenyl-*p*-benzoquinone systems was greater than that in the anthracene-*p*-benzoquinone system, which suggests that the *p*-benzoquinone molecules are adsorbed on the anthracene crystal more strongly than on the *p*-terphenyl crystal.

The adsorption of the acceptor molecules on the donor crystals was attributed most reasonably to charge-transfer interactions between them. Following Mulliken's suggestion,⁹ some attempts were made to elucidate adsorption phenomena in terms of charge-transfer interactions, but not successfully. As the charge-transfer theory is applied most successfully to

the problem of intermolecular interactions between neutral organic molecules in the homogeneous systems, the adsorption of organic molecules on organic molecular crystals is expected to be a good example of charge-transfer adsorption. In the present case, *p*-benzoquinone is considered to be bound to *p*-terphenyl or anthracene molecules at the surface, forming "surface charge-transfer complexes." Assuming a 1:1 composition of the complex, the stability of the surface complexes was compared to that of a complex formed in homogeneous media. The equilibrium for complex formation in a heterogeneous or homogeneous system is expressed as follows, respectively



where An and Q denote anthracene and *p*-benzoquinone, respectively, and the subscript s represents the surface substance. The equilibrium constant K_s , or K , is easily estimated, if the concentration of *p*-benzoquinone, $Q_{1/2}$, where half of the anthracene molecules are bound to the quinone, is known. K is equal to $Q_{1/2}^{-1}$ provided that the concentration of quinone is much larger than that of the complex. In this way K_s was evaluated to be about $7 \times 10^2 \text{ l. mol}^{-1}$. The corresponding values in homogeneous systems are unfortunately not known, but judging from the equilibrium constants of *p*-benzoquinone complexes with other aromatic hydrocarbons (for example, K for hexamethylbenzene-*p*-quinone in CCl_4 is $6 \times 10^{-1} \text{ l. mol}^{-1}$ at 18°) and those of complexes including electron acceptors, which have electron affinities comparable to or larger than that of *p*-benzoquinone¹⁰ (for example, K for anthracene-*p*-chloranil in CCl_4 is 7 l. mol^{-1} at 20°), they should be one order of magnitude smaller than K_s at most.

As is shown in Table II, a remarkable increase in I_{ps}^- was observed when *p*-phenylenediamine was added to the electrode, which indicates that the electron-transfer reaction occurred between the excited anthracene molecules at the surface of the crystal and the *p*-phenylenediamine molecules in the electrode, resulting in electron injection into the crystal from the electrode. The same effect was observed when phenothiazine was used in place of *p*-phenylenediamine, although the effect was not so large. A similar effect of aliphatic amines on the photoconductivity of a perylene crystal has been reported.¹¹

Electron-transfer reactions between excited aromatic hydrocarbons and various amines have been observed in homogeneous media by the measurement of fluorescence; the fluorescence of aromatic hydrocarbons is remarkably quenched in the presence of amines *via* electron-transfer reactions.¹² Similar reactions at the surface of the crystal would cause electron injection into the crystal.

Acknowledgment. The author wishes to express his gratitude to Professor K. Tamaru for his constant encouragement and helpful discussions.

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