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The Photo-induced Electron Transfer Reactions between Crystals of Aromatic Hydrocarbons and Quinones

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The photo-induced electron transfer reactions between crystals of aromatic hydrocarbons and several quinones were studied by measuring the increase of the photocurrent in the crystals due to the carrier injection from the ethanol electrode containing the quinones. The reaction rates were shown to be independent of sorts of quinones used when its concentration was sufficiently high. The excitation limited mechanism of the reaction was proposed to be consistent with this behavior and the observed concentration dependence of the reaction.

It has been reported previously[1,2] that the photo-induced electron transfer reaction occurs with high efficiency between a crystal of aromatic hydrocarbon and a π-electron acceptor dissolved in the liquid electrode contracted with the crystal. The rate of the electron transfer reaction is proportional to the saturation value of the photo-hole-current in the crystal which is attained by applying sufficiently high voltages.

In such cases as the photo-hole injection from tetrachloro-phthalonitrile into anthracene crystals, the saturation photocurrent depends linearly upon the concentration of added electron acceptor. On the other hand when *p*-benzoquinone is used as an acceptor, the saturation photocurrent begins to deviate from the linear dependence as the concentration increases and reaches a limiting value. This behavior was attributed tentatively to the electron transfer including *p*-benzoquinone adsorbed on the surface of the crystal.

It is reported in this paper that this feature is found generally in the photo-induced electron transfer reactions between the crystals of aromatic hydrocarbons and quinones with fairly high electron affinities, and the evidences which suggest another explanation for this behavior are presented

Experimental

The measuring procedures for the photocurrent in the crystals due to the photo-induced hole injection from the liquid ethanol electrode were the same as previously described[1] where the simplified type of Kallmann- and Popes' cell[3] was used. Thin platelets of single crystals of the aromatic hydrocarbons, anthracene, naphthacene, perylene, and *p*-terphenyl were prepared following the method previously reported.[2] All the quinones except *o*-chloranil were of com-

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

[2] A. Yamagishi and M. Soma, This Bulletin, **43**, 3741 (1970).

[3] H. Kallmann and M. Pope, *Rev. Sci. Instr.*, **30**, 44 (1959).

mercial source, purified by recrystallization and by sublimation if possible. *o*-Chloranil was synthesized according to Brook,[4] purified by recrystallization from carbon tetrachloride and by sublimation.

Results

Figure 1 shows changes in the saturation photo-hole-current in an anthracene single crystal with the concentration of *p*-chloranil added to the dark side (back face concerning to the direction of illumination) electrode. The crystal was excited by the light of wavelength at 4010 Å. As the back face electrode was positively biased, the observed photocurrent was attributed to the hole injection from the electrode, *i.e.* to the photo-induced electron transfer reaction between the excited anthracene crystal and *p*-chloranil. The saturation photocurrent reached to the certain limiting value as the concentration of *p*-chloranil increased. This behavior of concentration dependence of the photocurrent was already reported for the anthracene crystal/*p*-benzoquinone system,[1] and now, was found to be a general feature of the photo-induced electron transfer between excited aromatic hydrocarbons and various quinones. Figures 2a and 2b exemplify this behavior in the perylene crystal/*p*-benzoquinone, and the naphthacene crystal/*o*-chloranil systems. In these cases the crystals were illuminated at 5025 Å. Perylene and naphthacene have considerably lower ionization potentials than holes from the electrode to the crystal. The electron transfer reaction from the aromatic crystals to the quinones occurred without photo-excitation. In Figs. 2a and 2b, the concentration dependence of the dark injection was shown for comparison. They are quite different from those of the photo-injection. The dark currents were almost proportional to the concentration of the added electron acceptors in the concentration range studied.

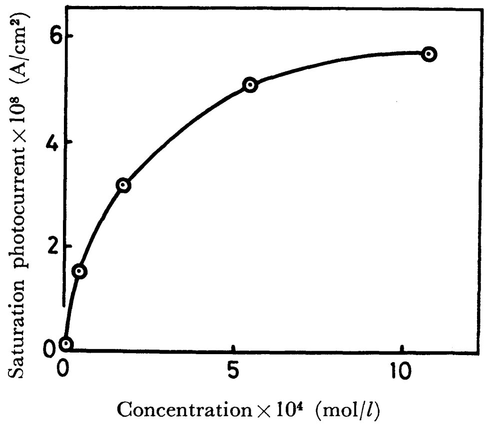
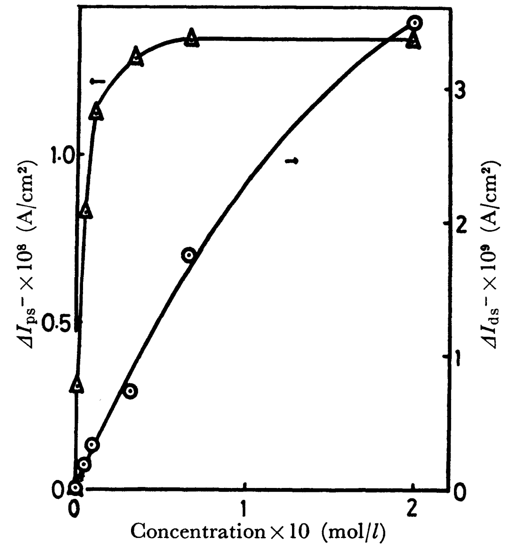
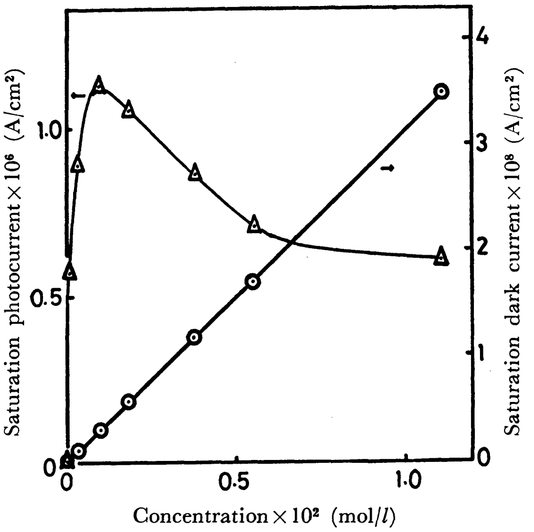


Fig. 1. Changes in the saturation photocurrent in anthracene crystal with the concentration of added *p*-chloranil. Electrode arrangement, water | crystal | ethanol + *p*-chloranil, water electrode illuminated by 4010 Å light, ethanol electrode biased positive.

This fact suggests that there might be specific circumstances causing the appearance of the limiting values in the photocurrents but not in the dark current. To get more information about the phenomena, the photo-induced electron transfer reactions with various quinones as electron acceptor were compared. Two types of comparison were made.



a) perylene crystal/*p*-benzoquinone system excited by 5020 Å



b) tetracene crystal/*o*-chloranil system excited by 5020 Å

Fig. 2. Changes in the saturation photo-(ΔI_{ps}^-) and dark (ΔI_{ps}^-) current in the aromatic hydrocarbons with the concentration of the added acceptors.
Electrode arrangements were the same with Fig. 1.

The relative limiting values of the saturation photo-hole current in an anthracene crystal with four quinones as electron acceptor are shown in Table 1. In the last column are the reduction potentials of the quinones[5] which are the measure of their electron affinities in the polar organic solvents. The limiting values were attained at the lower concentrations of the acceptor, the larger the electron affinity (smaller the reduction potential) of the acceptor was. Although the electron affinity varies in fairly wide range

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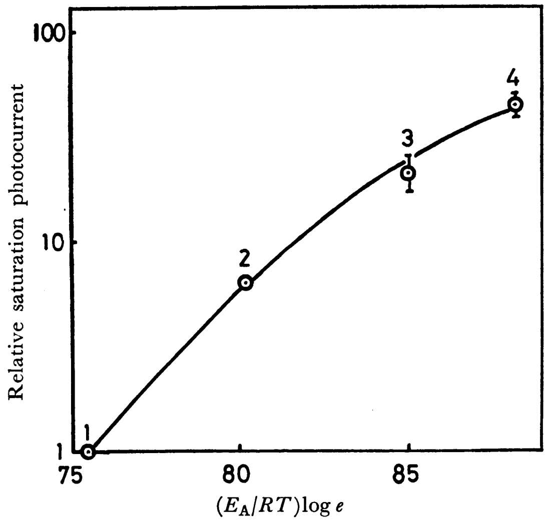
[4] A. G. Brook, *J. Chem. Soc.*, **1952**, 5040.

[5] Data sited in G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

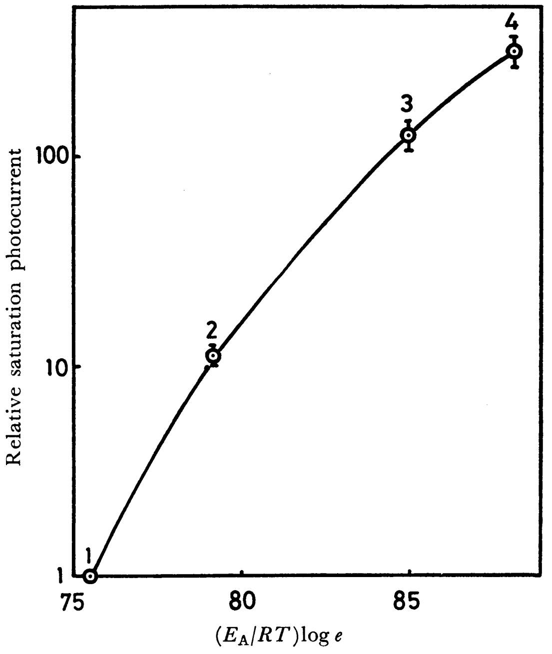
TABLE 1. RELATIVE LIMITING VALUES OF THE INCREASE IN THE PHOTO-HOLE-CURRENT (ΔI_{ps}) FOR THE ANTHRACENE CRYSTAL/QUINONE SYSTEMS[a)]

Acceptor	Concentration mol/l	Relative limiting value of ΔI_{ps}	Reduction potential[5)] $E_{1/2}^{red}$ (volts)
p-chloranil	1.62×10^{-3}	1	−0.01
2,6-dichloro-*p*-benzoquinone	6.02×10^{-3}	0.93—1.04	0.18
p-benzoquinone	1.56×10^{-2}	0.86—0.91	0.51
1,4-naphtoquinone	2.28×10^{-2}	0.77—0.78	0.71

a) Electrode arrangement, water|crystal|ethanol+quinone, water electrode illuminated by 4010Å light, ethanol electrode biased positive.



a) anthracene crystal/quinone systems excited by 4010 Å light.



b) tetracene crystal/quinone systems excited by 5020 Å light.

Fig. 3. Dependence of the saturation photocurrent upon the electron affinity(E_A) of the quinones. The photocurrent was normalized per unit concentration. Electrode arrangements were the same with Fig. 1.

among the quinones used, the differences in the limiting values of the photocurrents were small. The limiting values of the photocurrents in the naphthacene crystal with *p*-chloranil and 2,6-dichloro-*p*-benzoquinone as acceptors were also roughly the same, while with *p*-benzoquinone it gave substantially smaller limiting value (one third or one fourth of the former). The latter might be attributed, at least partly, to the presence of another concentration effect which caused the photocurrent to decrease below the limiting value with further increasing the concentration as was the case in the naphthacene crystal/*o*-chloranil system shown in Fig. 2b.

The second comparison was made in the small concentration region where the photocurrent was almost proportional to the concentration of the electron acceptor. In Fig. 3, the relative saturation photocurrents normalized per unit concentration in anthracene and naphthacene crystals are plotted aginst the electron affinities of the various quinones.

Discussion

The saturation photocurrent I_{ps} attained by applying sufficiently high voltage can be related to the number of holes, n, injected per unit time by the following equation.

$$n = \frac{F}{q} I_{ps} \tag{1}$$

where F is Faraday constant and q is the charge of an electron. Accordingly, changes in the saturation photo-hole-current upon the addition of the electron acceptor are the direct measure of the rate of the electron transfer reactions between the excited crystal and the electron acceptor. The rate of the photo-induced electron transfer reaction was shown to have a different concentration dependence from that of the electron transfer reaction in the dark. It reached a limiting value.

In the case of the anthracene crystals the limiting value was almost independent of the acceptor as demonstrated in Table 1. The steady state for the concentration of the excited molecule M* in the lowest singlet excited state in the surface molecular layer of the crystal might be expressed as follows

$$p - \{k_f + k_d + k_e[\mathrm{A}]\}[\mathrm{M}^*] = 0, \tag{2}$$

where k_f is the fluorescence life time of M*, k_d nonradiative decay constant of M*, k_e rate constant of the electron transfer reaction between M* and the acceptor molecule A, [A] the concentration of the acceptor molecule, and p is the rate of the production of the excited molecule M* at the surface, including those produced by direct excitation and by excitation migration. The rate of electron transfer reaction, $R=k_e\cdot$[A][M*], therefore, using Eq. (2) is expressed by

$$R = \frac{k_e p[\mathrm{A}]}{k_f + k_d + k_e[\mathrm{A}]} \tag{3}$$

If the concentration of the acceptor is sufficiently high, so that $k_e[\mathrm{A}] \gg k_f + k_d$, R reaches to the limiting value as was experimentally observed. In these cases, the rate is limited by the rate of the production of the excited molecules, p. Equation (3) can also be expressed in the following form

$$\frac{[\mathrm{A}]}{R} = c_1 + c_2[\mathrm{A}], \tag{4}$$

where c_1, c_2 are constants. This type of concentration dependence of R,*i.e.* concentration dependence of the saturation photo-hole-current was reported previously in the case of the anthracene crystal/*p*-quinone system[1] and now proved to be generally the case as exemplified by the anthracene/*p*-chloranil system (Fig. 1). It was attributed tentatively to the formation of the adsorbed layer of the acceptor molecule. However, the present with the acceptor-independent limiting value of the saturation photo-current is preference of the excitation limited mechanism.

The electron transfer reaction from excited anthracene crystal to organic electron acceptors were shown to be a very efficient process.[1,2] In fact, the limiting values of the saturation photocurrent in the anthracene and naphthacene crystal were at least several times as large as the photocurrent due to the photo-induced hole injection from the aqueous electrode, whereas the quantum efficiencies for the hole injection were reported to be 0.033 (at 3650Å)[6] and 0.075 (at 5050Å)[7] respectively.

The relative photo-currents in the smaller concentration region are the direct measure of the rate constant, k_e, of the electron transfer reaction between the excited aromatic molecule at the surface and the quinones, if the reaction is assumed to occur *via* direct collision of the excited molecule and the electron acceptors. In this case the rate constant may be expressed in the conventional equation.

$$k_e = Z \exp(-\Delta F^{\ddagger}/RT) \tag{5}$$

where Z is the collision number and $\Delta F^{\ddagger}$ is the free energy of activation. On the other hand, the standard free energy of the reaction ΔF° is expressed as follows

$$\Delta F^\circ = I_c - E_a - E_x \tag{6}$$

where I_c is the ionization potential of the crystal, E_a is electron affinity of the quinone including the solvation energy, and E_x is the energy supplied by light. For the same crystal only E_a is changed in Eq. (6) from one acceptor to another. The collision number Z in Eq. (5) can be reasonably assumed to be the same for all the quinones used. In such circumstances, Figs. 3a and 3b represent the relation between the rate constant or the free energy of activation and the changes in the standard free energy of reaction. The observed increase in the rate constant with the increasing electron affinity of the acceptor is in accordance with trend of the efficiency of acceptors in quenching the fluolescence of aromatic hydrocarbons in solution *via* the electron transfer reaction.[8]

The larger the reaction rate constant, the limiting value was attained at the lower concentration of the acceptor, which is again consistent with Eq. (3).

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[6] H. Kallmann and M. Pope, *Nature*, **185**, 753 (1960).

[7] N. Geacintov, M. Pope, and H. Kallmann, *J. Chem. Phys.*, **45**, 2639 (1966).

[8] A. Nakajima and H. Akamatu, This Bulletin, **41**, 1961 (1968).