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## PHOTO-INDUCED ELECTRON TRANSFER FROM ORGANIC CRYSTALS TO BIOLOGICALLY INTERESTING SUBSTANCES

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SUMMARY

1. The d.c. photoconductivity of organic molecular crystals was studied using liquid electrodes containing model compounds of the coenzymes to elucidate the effect of these additives on the rate of electron transfer from the crystals to the electrodes. The number of injected holes per unit time is the measure of the rate of the electron transfer.

2. Compounds containing the pyridinium cation nucleus enhanced the rate of the electron transfer reaction between excited anthracene molecules and the electrodes. On the addition of *N*-benzyl nicotinamide chloride to the aqueous electrode, the photocurrent was observed to increase several fold.

3.  $\text{Ag}^+$  had similar effects on the photoconductivity of anthracene crystals.

4. Excited riboflavin molecules act as electron acceptors for crystals of the aromatic hydrocarbons. When riboflavin molecules and silver ions were added to the aqueous electrode, a remarkable increase in the hole current was observed. The effect was more than additive.

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## INTRODUCTION

In our previous report<sup>1</sup> the photo-induced electron transfer reaction between the crystals of aromatic hydrocarbons and other organic molecules was observed as an increase in the photocurrent by carrier injection from the liquid electrode containing organic molecules, and we mentioned its possible correlation to the primary processes in photosynthesis or other situations involving electron transfer in living cells in a manner similar to that first proposed by CALVIN<sup>2</sup>. In this report we attempted to extend the previous work to the electron transfer reaction including biologically interesting substances. We chose such model compounds of nicotinamide coenzyme and flavin coenzyme as are listed in Fig. 1. Both coenzymes play an important role in the electron transport processes in living cells. The one important aspect of the photosynthesis situation is that  $\text{NADP}^+$ , the nicotinamide coenzyme, which has a low redox potential, acts as a final acceptor of electrons transferred from chlorophyll *a*, in which the electrons are raised to an excited state by the light absorption and thus reduce  $\text{NADP}^+$ . The reduction of the molecule with a low redox potential or small electron affinity by the photo-excited electron in the donor molecule is just what

would occur in a photo-induced electron transfer reaction at the surface of an organic crystal. The function of the flavin coenzyme as an electron carrier is often stimulated by the coexistence of certain metal ions<sup>3</sup>. Accordingly, we examined the effect of addition of metal ions on the electron transfer reaction between organic crystals and riboflavin molecules.

#### METHODS AND MATERIALS

Experimental procedures were similar to those previously reported<sup>1</sup>. Single crystals of anthracene and *p*-terphenyl were obtained either by sublimation in a fused tube or by crystallization in solution. Nicotinamide and riboflavin of commercial G. P. grade were used. *N*-Benzylnicotinamide chloride was synthesized from nicotinamide and benzyl chloride.

In the measurement of the d.c. photocurrent, tungsten lamps were used as light sources. The wavelength was selected by metal-interference filters. The intensity of incident light was varied by changing the applied voltage for the tungsten filaments.

#### RESULTS

##### *Increase of the saturation photocurrent in anthracene crystal in the presence of pyridinium ions*

Table I shows the saturation d.c. photocurrent in an anthracene single crystal when the positive aqueous electrode containing nicotinamide molecules was illuminated. The saturation in the photocurrent was attained by applying sufficiently high voltages so that the photocurrent was limited by the rate of the hole injection from the electrode<sup>1,4,5</sup>. In this experiment the pH of the electrode solution was varied by the addition of HCl and KCl (Clark-Lubs' buffer). The solution of pH 7.9 is the aqueous solution of nicotinamide of the given concentration. In the acidic condition almost all the nicotinamide molecules were in their protonated forms having a pyridinium ion ring.

TABLE I

EFFECTS OF ADDED NICOTINAMIDE ON THE RATE OF HOLE INJECTION INTO AN ANTHRACENE CRYSTAL FROM THE AQUEOUS ELECTRODE

Nicotinamide was added to the illuminated electrode.

Nicotinamide concn. (M)	Conditions of the electrode	Saturation photocurrent* $I_{ps}^+ \times 10^8$ (A)
0	pH 7.0	1.5
0	Acidic (pH 1.67)	1.5
0.0230	pH 7.85	1.2
0.0149	Acidic	2.6
0.0298	Acidic	3.1
0.0595	Acidic	3.0
0.119	Acidic (pH 3.7)	2.5

\* Electrode area,  $3 \cdot 10^{-2}$  cm<sup>2</sup>; incident light, 4010 Å.

In Table II the effect of added *N*-benzylnicotinamide chloride on the saturation photocurrent is shown. An approximately 8-fold increase was obtained when 4 mM of *N*-benzylnicotinamide chloride was added to the electrode. Other compounds which have a pyridinium ion nucleus as shown in Fig. 1 had an effect similar to that given by protonated nicotinamide or *N*-benzylnicotinamide chloride, although the effect was not so pronounced. Ethanol solutions of these compounds with a pyridinium ion nucleus, though the solubility is small, affected the photoconductivity similarly.

TABLE II

EFFECTS OF ADDED *N*-BENZYLNICOTINAMIDE CHLORIDE ON THE RATE OF HOLE INJECTION INTO AN ANTHRACENE CRYSTAL FROM THE AQUEOUS ELECTRODE

*N*-Benzylnicotinamide was added to the illuminated electrode.

<i>N</i> -Benzylnicotinamide concn. ( <i>M</i> )	Saturation photocurrent* $I_{ps}^+ \times 10^8$ (A)
0	1.4
$1.2 \cdot 10^{-5}$	2.6
$3.6 \cdot 10^{-5}$	4.9
$1.3 \cdot 10^{-4}$	9.8
$4.3 \cdot 10^{-3}$	11.8

\* Electrode area,  $3 \cdot 10^{-2} \text{cm}^2$ ; incident light, 4010 Å.

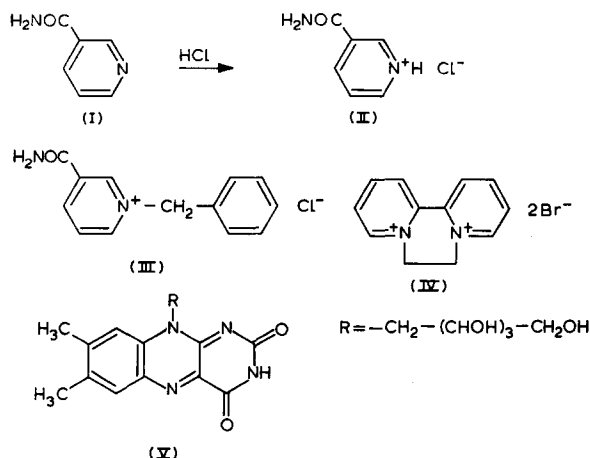


Fig. 1. (I) nicotinamide; (II) nicotinamide hydrochloride; (III) *N*-benzylnicotinamide chloride; (IV) 6,7-dihydrodipyrido[1,2-*a*:1',2'-*c*]pyrizedinium dibromide; (V) riboflavin.

### Effect of added riboflavin

Riboflavin is slightly soluble in ethanol and its saturated solution used as a dark-side electrode biased positive gave no changes in the saturation photocurrent  $I_p^+$  compared to that for the ethanol electrode without riboflavin. In acidic ethanol riboflavin is more soluble and acts as a stronger oxidant<sup>6</sup>. The increase in the photo-

\* We use the notation  $I_p^+$  for the photocurrent when the illuminated electrode was biased positive and  $I_p^-$  when the illuminated electrode was biased negative, *i.e.* the dark-side electrode biased positive.  $I_{ps}$  represents the saturation photocurrent.

current when the riboflavin was added to the electrode of ethanol saturated with HCl is illustrated in Fig. 2. The addition of riboflavin in the dark-side electrode resulted in a 2-fold increase in the saturation photocurrent  $I_{ps}^-$  but no change in the photocurrent  $I_p^+$ . A similar effect was found when an aqueous solution of riboflavin was used as an electrode. The changes in the spectral dependence of the saturation

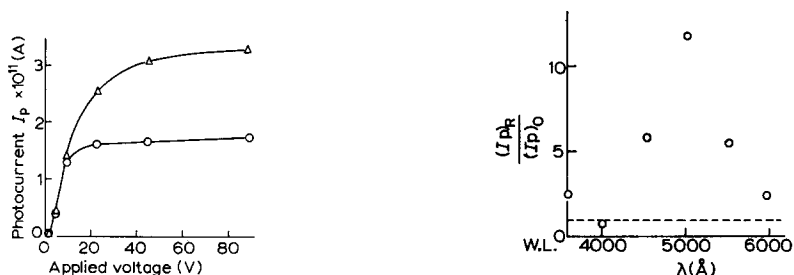


Fig. 2. Hole photocurrents in anthracene crystals when the dark-side electrode of acidic ethanol was biased positive. The illuminated electrode was aqueous. O, without riboflavin;  $\Delta$ , with saturated riboflavin.

Fig. 3. Changes in the spectral response of the saturation photocurrent ( $I_{ps}^-$ ) in anthracene crystals by addition of riboflavin to the aqueous dark-side electrode.  $(I_p)_R / (I_p)_0$  is the ratio of the photocurrents after and before the addition of riboflavin. W. L. denotes the excitation by white light.

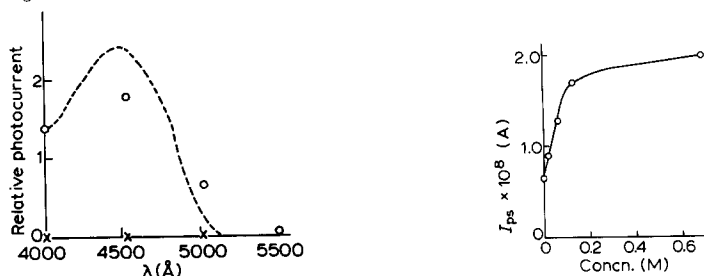


Fig. 4. Spectral dependence of the saturation photocurrent ( $I_{ps}^-$ ) in *p*-terphenyl crystal. O, with riboflavin in the aqueous dark-side electrode; X, without riboflavin. Dotted line shows the absorption spectrum of an aqueous solution of riboflavin.

Fig. 5. Changes in the saturation photocurrent ( $I_{ps}^+$ ) in anthracene crystal on addition of  $\text{AgNO}_3$  to the illuminated aqueous electrode. The crystal was excited by white light.

photocurrent  $I_{ps}^-$  caused by the addition of riboflavin are shown in Fig. 3. Fig. 4 shows the spectral dependence of the normalized saturation photocurrent  $I_{ps}^-$  in a *p*-terphenyl crystal for the electrode of aqueous riboflavin solution. The absorption spectrum of an aqueous solution of riboflavin is also shown for comparison. The photocurrent for the electrode without riboflavin was negligible in the spectral region corresponding to the absence of any absorption band of the *p*-terphenyl crystal.

#### *The effect of added metal ions on the photocurrent sensitized by riboflavin*

When certain metal salts were added to the positive aqueous electrode, the saturation photocurrent in anthracene crystals was increased as shown in Fig. 5 ( $\text{Ag}^+$ ) and Table IV ( $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ ). Fig. 5 shows the changes in the saturation photocurrent  $I_{ps}^+$  with the concentration of added  $\text{AgNO}_3$ . The addition of  $\text{AgClO}_4$  resulted in a quite similar effect.

TABLE III

CHANGES IN THE SATURATION HOLE PHOTOCURRENT IN AN ANTHRACENE CRYSTAL ON THE ADDITION OF RIBOFLAVIN AND SILVER NITRATE TO THE ELECTRODE

Riboflavin and  $\text{AgNO}_3$  were added to the dark-side electrode.

Riboflavin concn. (M)	$\text{AgNO}_3$ concn. (M)	Saturation photocurrent* $I_{ps} \times 10^{11}$ (A)
0	0	85
$2.23 \cdot 10^{-4}$	0	210
0	$1.20 \cdot 10^{-1}$	130
$2.23 \cdot 10^{-4}$	$1.16 \cdot 10^{-1}$	5100
$2.23 \cdot 10^{-4}$	$2.32 \cdot 10^{-2}$	4800
$2.23 \cdot 10^{-4}$	$4.64 \cdot 10^{-3}$	4500
$4.46 \cdot 10^{-5}$	$2.32 \cdot 10^{-2}$	2080
$8.92 \cdot 10^{-6}$	$4.64 \cdot 10^{-3}$	1070

\* Electrode area,  $3 \cdot 10^{-2} \text{ cm}^2$ ; incident light was white light from a 750-W tungsten lamp.

TABLE IV

CHANGES IN THE SATURATION HOLE CURRENT IN AN ANTHRACENE CRYSTAL ON THE ADDITION OF RIBOFLAVIN AND  $\text{FeCl}_3$  OR  $\text{CuCl}_2$  TO THE ELECTRODE

Riboflavin and the metal chlorides were added to the dark-side electrode.

Riboflavin concn. (M)	Chloride concn. (M)	Saturation photocurrent* $I_{ps} \times 10^{10}$ (A)
0	0	3
$2.23 \cdot 10^{-4}$	0	4.5
0	$\text{FeCl}_3$ 0.1	6.6
$2.23 \cdot 10^{-4}$	$\text{FeCl}_3$ 0.1	24
0	$\text{CuCl}_2$ 0.4	4.2
$2.23 \cdot 10^{-4}$	$\text{CuCl}_2$ 0.4	19

\* Incident light was white light from a 750-W tungsten lamp.

When both the metal salt and riboflavin were dissolved in the positive electrode, a pronounced increase in the saturation photocurrent was observed as exemplified in Tables III and IV. The effects were more than additive.

## DISCUSSION

### *Increase of the saturation photocurrent in anthracene crystal in the presence of pyridinium ions*

The model compounds of nicotinamide coenzyme which have a pyridinium ion nucleus increased the saturation photocurrent in an anthracene crystal as was exemplified in Tables I and II. Since the sensitization occurred only when the electrode containing these compounds was biased positive, the effect of the added compounds was to enhance the hole injection into the anthracene crystal. The hole injection from the pure water electrode without sensitizer into the anthracene crystal occurs *via* the electron transfer reaction between the surface anthracene molecule in its

lowest singlet excited state and the water molecule<sup>4,5</sup>. The sensitized saturation hole current was linearly dependent on the light intensity, and its spectral dependence was the same as that of the saturation photocurrent in the anthracene crystal without the sensitizers. Accordingly, the photo-induced electron transfer reaction between the anthracene molecule at the surface of crystal and the electrode with the sensitizer is expressed as



or



where  $\text{An}^*$  is an excited anthracene molecule, S is the sensitizer and  $(\text{H}_2\text{O})^-$  is a water molecule in the electrode. In Eqn. 1, the sensitizer acts as a final electron acceptor, while in Eqn. 2 it participates at the intermediate step in the electron transfer from the excited anthracene to a water molecule. In every way the effect of the added sensitizers seems to correlate with the electron-accepting property of pyridinium ions, which is consistent with the fact that nicotinamide itself did not affect the photocurrent at all in the absence of a proton at the ring nitrogen. It is of interest to note that nicotinamide coenzyme which acts as an electron acceptor in the biological electron transfer processes also has a pyridinium ion nucleus.

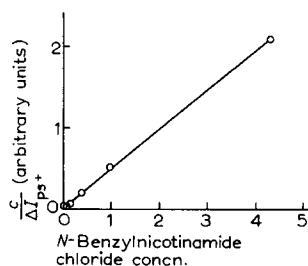


Fig. 6. Langmuir-type plot for the increase in the saturation photocurrents ( $\Delta I_{ps}^+$ ) in anthracene crystal versus the concentration of *N*-benzylnicotinamide chloride added to the aqueous illuminated electrode. Excitation light, 4010 Å.

The changes in the saturation photocurrent with the concentration of added *N*-benzylnicotinamide chloride indicate that the sensitizer is adsorbed on the surface of the anthracene crystal to form the surface complex. This is clearly shown in Fig. 6 where the increase in the saturation photocurrent was plotted in the analogous form of the Langmuir adsorption isotherm. The formation of surface complexes was already known in the case of the benzoquinone-anthracene system<sup>1</sup>.

#### *Increase of the saturation photocurrent in the anthracene crystals in the presence of riboflavin and metal ions*

The photo-induced electron transfer reaction between anthracene and riboflavin brings an enhancement of the saturation hole photocurrent in the anthracene crystal when the riboflavin is added to the electrode. Contrary to the case with the pyridinium ions, the electron transfer takes place between the excited riboflavin and the anthracene in its normal state as is indicated by the spectral dependence of the sensitized photocurrent (Fig. 3). This situation is more clearly shown in the case of the

riboflavin-*p*-terphenyl system where only a negligible photocurrent was observed without the additive in the spectral range studied (above 4000 Å). An example of electron transfer from organic crystals to an excited electron acceptor such as quinone was reported previously<sup>1</sup>. The electron acceptor molecule in its excited electronic state has a greater electron affinity than in its ground state because of the excitation energy, as the excited donor acts as a stronger donor than in its ground state. Thus the redox reactions which cannot occur in the dark can proceed photochemically and the light energy is converted to so-called chemical energy in the form of strong oxidants and reductants.

Silver ion is known to form addition complexes of charge-transfer type with aromatic hydrocarbons<sup>7</sup>. In this case silver ion acts as a weak electron acceptor. The increase in the saturation hole photocurrent in the anthracene crystal is probably due to the electron transfer from the excited anthracene molecules to the adsorbed silver ions, as is indicated by the concentration dependence of the sensitized photocurrent (Fig. 5). The effect of the other metal salts such as FeCl<sub>3</sub> and CuCl<sub>2</sub>, though not so pronounced as that of the Ag<sup>+</sup>, can also be attributed to their electron-accepting properties.

The combined effect of the metal ions and riboflavin is interesting especially in connection with the role of metal ions in the reactions catalyzed by flavin enzymes. The addition of both riboflavin and metal ions to the electrode increased the saturation photocurrent more than the sum of the effect of each sensitizer. The Ag<sup>+</sup>-riboflavin system gave a remarkable combined effect. Ag<sup>+</sup> forms a 1:1 complex with riboflavin having an electronic structure similar to a protonated riboflavin semiquinone<sup>8</sup>. The spectral dependence of the sensitized photocurrent essentially followed the absorption spectrum of an Ag<sup>+</sup>-riboflavin complex. Under the conditions given in Table III, most of the riboflavin molecules are combined with Ag<sup>+</sup> and the photocurrent is independent of the concentration of Ag<sup>+</sup>. Accordingly, the excited Ag<sup>+</sup>-riboflavin complex acts as an electron acceptor. In the case of sensitization by riboflavin and ferric or cupric salts, the spectral dependence was similar to the photocurrent sensitized by riboflavin alone, but whether the interaction of the metal ions with anthracene or with riboflavin is responsible for the combined effect is not clear.

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