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Organic Charge Transfer Salts. III.$^{1)}$ Photoconductive and Magnetic Properties of Organic Charge Transfer Salts

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The photoconductive and semiconductive properties of some organic charge-transfer (CT) salts consisting of a pyrylium or thiopyrylium cation and a polycyanoacid anion were investigated in single crystals. The salts are poor semiconductors with a resistivity of 10^{10}—10^{12} ohm·cm at room temperature, but show relatively large photoconduction when irradiated with monochromatized light in the interionic CT absorption band. There is a strong possibility that the photocarrier is intrinsic in nature, being generated spontaneously from the excited CT state. A weak ESR signal observed originally in these salts increased on the CT band or near IR excitation. From the relationship between the darkcarriers, photocarriers, paramagnetic species and the excited CT state, a mechanism of electrical conduction is proposed in which the carrier generation by the CT interaction and the carrier migration by trapping conduction are involved.

Organic charge-transfer (CT) salts are a class of ionic compounds consisting of organic cation and anion, having CT interaction between the component ions. In order to elucidate the role of the interionic CT interaction in them, we have studied the physical properties$^{1,2)}$ of new organic CT salts consisting of a pyrylium or thiopyrylium cation and a polycyanoacid anion (Fig. 1). We have investigated the photoconductive and semiconductive properties as well as the magnetic properties.

Although photoconduction has been found in several weak molecular CT complexes having low dark conductivity,$^{3-6)}$ the photocarrier generation in most cases has been considered to be extrinsic in nature, an intrinsic carrier generation not being proved in any of the cases. With weak molecular CT complexes, Akamatu and Kuroda discussed the relationship between the conduction state and the excited CT state.$^{3)}$ They suggested that a difference of energy equivalent to that necessary for the separation of the excited CT state into free ions, that is, the separation of a $\mathrm{D}^{\dot{+}}\mathrm{A}^{\dot{-}}$ ion-radical pair into two charge carriers might prevent the intrinsic carrier generation. However, in the case of an interionic CT salt, the excited CT state might consist of two neutral radical species, D·A·, and the carrier separation from the CT state would be easier than in the case of a weak molecular CT complex. Thus, in an organic CT salt, the possibility of intrinsic carrier generation by the CT excitation is expected.

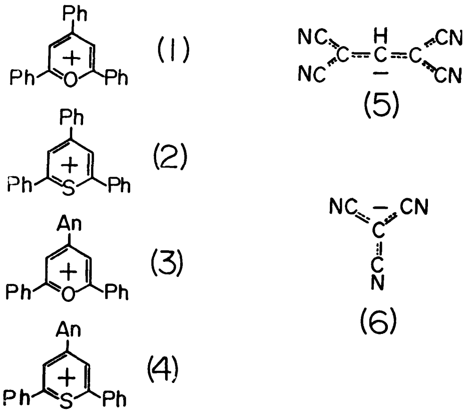

Fig. 1. (1) 2,4,6-triphenylpyrylium (TPP) cation, (2) 2,4,6-triphenylthiopyrylium (TPT) cation, (3) 4-anisyl-2,6-diphenylpyrylium (ADPP) cation, (4) 4-anisyl-2,6-diphenylthiopyrylium (ADPT) cation, (5) 1,1,3,3-tetracyanopropenide (TCP) anion, (6) tricyanomethanide (TCM) anion.

Actually, all the CT salts studied showed a photocurrent about ten times larger than the dark current on irradiation at the CT absorption band. A weak ESR signal, which seems to originate from the charge carriers in the dark conduction, was enhanced on the CT and near IR excitations. From the results obtained on the electrical and magnetic properties, we will discuss the mechanism of electrical conduction and the possibility of the intrinsic carrier generation in organic CT salts.

Experimental

Materials. Crystals of the organic CT salts(Fig. 1) were prepared as described previously.$^{2)}$ The salt was purified by recrystallization at least three times. Vacuum sublimation or zone refining could not be used because of decomposition of the salt. Single crystals of the CT salts, dimensions about $2\times1\times0.5$ mm, were grown from methanol–water (4 : 1) or methanol solution. However, except for TPT-perchlorate, single crystals of the perchlorate salts of other cations could not be obtained.

Conductivity Measurement. The apparatus for the measurement of the dark- and photo-conduction is shown in Fig. 2. The DC conductivity was measured with a Takeda-Riken vibrating reed electrometer, type TR-81. Temperature was controlled by passing cold nitrogen gas or heated air around a single crystal sample, and was monitored with a thermocouple. The light from a 500 W Xe lamp, arc current 20 A, was monochromatized with a monochromator. The energy distribution and the absolute light intensity of the Xe lamp were shown previously.$^{7)}$ In order to investigate

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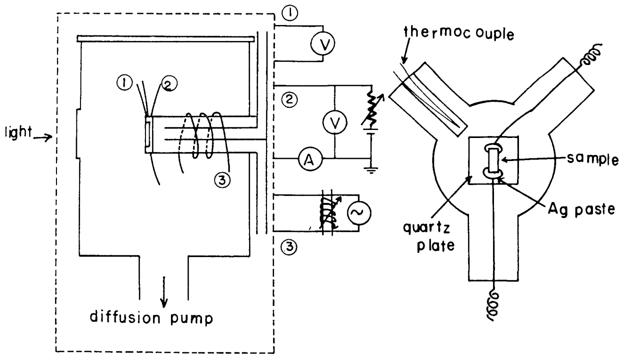

Fig. 2. Apparatus for the conductivity measurements.

the light intensity dependence of the photocurrent, neutral filters of known transmittance were inserted between a sample and a monochromator. A single crystal was placed on a quartz plate with Ag paste, which was used as electrodes (Fig. 2). In the case of TPP-perchlorate, a compressed pellet of powder crystals was used. The voltage-current characteristics were ohmic in all samples up to 200 V applied voltage, no photovoltaic current being observed when no voltage was applied. This indicates that the choice of electrode is adequate, and carrier injection from or to the Ag paste electrode is negligible. All conductivity measurements were performed both in dry air at one atmosphere and in a vacuum at 10^{-4}—10^{-5} mmHg.

ESR Measurement. The electron spin resonance measurement was carried out with an X band, JES-ME2X type spectrometer (Japan Electron Optics Laboratory Co. Ltd.) with a double mode cavity. A microcrystalline sample was packed in a quartz tube in air and in a vacuum at 10^{-2} mmHg. The concentration of unpaired spins of a salt was estimated by comparing its intensity with that of a DPPH sample. DPPH(Wako, pure grade) was purified by repeated recrystallizations from CS_2 or petroleum ether (a fraction of bp< 40 °C) solutions. The benzene solution or the powder sample dispersed in KCl (Merck, ultra pure grade, dried over 2 days at 200 °C in vacuum) was used as a reference substance of known concentration of unpaired spins. Temperature was varied by passing cold nitrogen gas or heated air into the cavity, and was monitored with a thermocouple attached around a sample tube in the cavity. The g-value of the unpaired spins in a salt was determined from the g-value of Mn^{2+} in a MgO sample.[8] For the measurement of photo-ESR absorption, a 500 W Xe lamp of 20 A was used. The spectral dependence of photo-ESR absorption was roughly estimated by combining several color glass filters of known transmittance at various wavelengths, since the light from a monochromator was too weak for observation of ESR absorption change.

Results

Dark Conductivity and Photoconductivity. The organic CT salts are semiconducting with resistivity in the range 10^{10}—10^{12} ohm·cm at room temperature. On irradiation with a visible light, a photocurrent of *ca.* 10 times greater magnitude than the dark current was observed.

The light intensity dependence of the photocurrent obeyed $i_{ph}=a\cdot L^n$, where L is the incident light intensity, a and n are the constants. This relation is given in Fig. 3 and the results in Table 1. The value of n appears to be independent of the presence of air, being 0.5 for all salts.

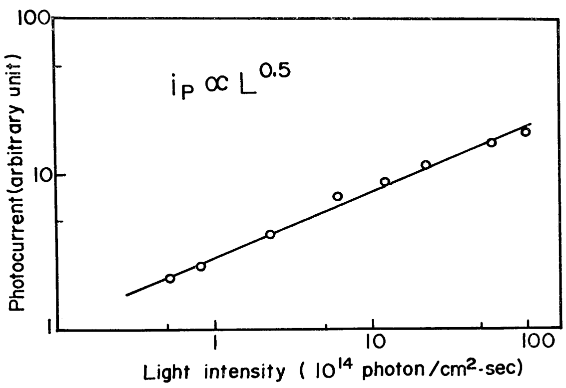

Fig. 3. Light intensity dependence of photocurrent at 650 nm of TPT-TCP salt.

Table 1. Light intensity dependence of photocurrent of organic CT salts

Salts	n in $i_{ph}=a\cdot L^n$		λ_{ex} (nm)[a]
	in vacuum	in air	
TPP-TCP	0.5	0.5	600
TPT-TCP	0.6	0.5	650
TPP-TCM	0.6	0.8	600
TPT-TCM	0.7	0.7	650
ADPP-TCP	—	0.6	600
ADPT-TCP	—	0.5	600
ADPP-TCM	—	0.5	600
TPT-ClO_4	0.4	0.4	500

a) wavelength of illuminating light.

The spectral dependence of the photoconduction is shown in Figs. 4 (a—d) for several salts, together with the corresponding absorption spectra. Large absorption bands near 400 nm are the locally excited (LE) bands of the component ions.[2] A relatively weak and broad absorption band observed near 550 nm in each CT salt but not in the corresponding perchlorate salt of the cation is assigned to the interionic

Table 2. Specific resistivity (ρ_d) in the dark at room temperature, photoconduction maximum wavelengths (λ^{ph}_{max}) and absorption maximum wavelengths (λ^{ab}_{max}) of organic CT salts

Salts	ρ_d (ohm·cm)	λ^{ph}_{max} (nm)	λ^{ab}_{max} CT band[a]	(nm) LE band[b]
TPP-TCP	10^{11}	640, 500	565	410
TPT-TCP	10^{11}	640, 500	540	390
TPP-TCM	10^{10}	580	530	410
TPT-TCM	10^{11}	600	520(S)[d]	390
ADPP-TCP	10^{12}	580, 520	530(S)	435
ADPT-TCP	10^{10}	620, 520	560(S)	430
ADPP-TCM	10^{11}	630, 520	520(S)	435
TPP-ClO_4[c]	10^{12}	500	—	410
TPT-ClO_4	10^{12}	500	—	390

a) measured by diffuse reflectance spectrum in solid state. b) the lowest LE band of the cation in absorption spectrum in CH_3OH solution. c) measured in a compressed pellet of powder crystals. d) shoulder.

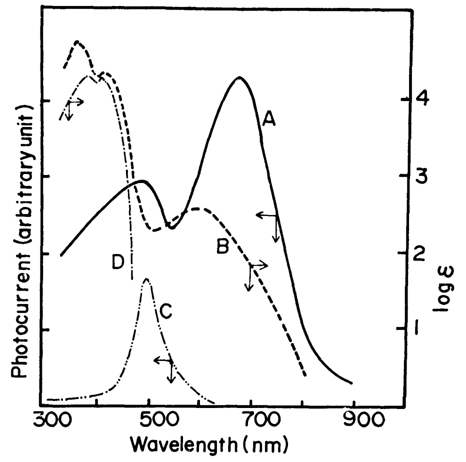

Fig. 4a. Spectral dependence of photocurrent and absorption spectra of TPP-TCP and TPP-perchlorate salts.

(A) photoconduction spectrum of TPP-TCP, (B) absorption spectrum of TPP-TCP in $CHCl_3$ solution, (C) photoconduction spectrum of TPP-ClO_4, (D) absorption spectrum of TPP-ClO_4 in CH_3OH solution.

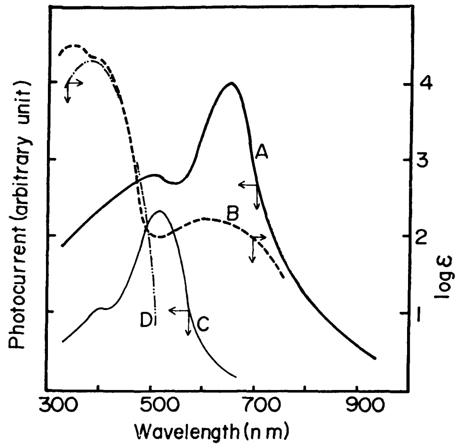

Fig. 4c. Spectral dependence of photocurrent and absorption spectra of TPT-TCP and TPT-perchlorate salts.

(A) photoconduction spectrum of TPT-TCP, (B) absorption spectrum of TPT-TCP in $CHCl_3$ solution, (C) photoconduction spectrum of TPT-ClO_4, (D) absorption spectrum of TPT-ClO_4 in CH_3OH solution.

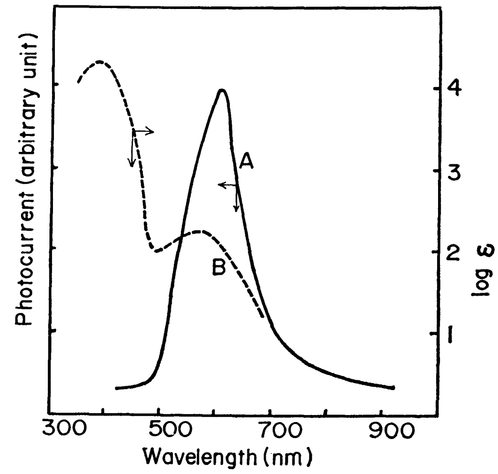

Fig. 4b. Spectral dependence of photocurrent and absorption spectrum of TPP-TCM salt.

(A) photoconduction spectrum, (B) absorption spectrum in $CHCl_3$ solution.

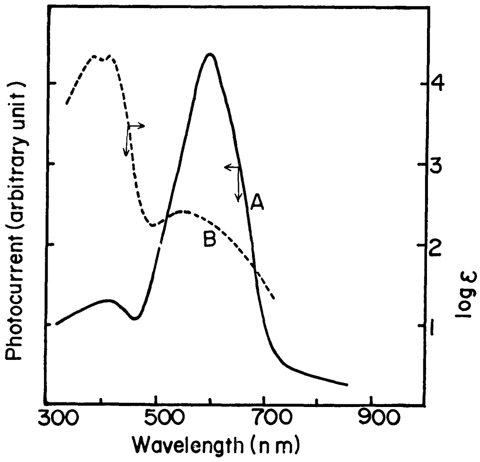

Fig. 4d. Spectral dependence of photocurrent and absorption spectrum of TPT-TCM salt.

(A) photoconduction spectrum, (B) absorption spectrum in $CHCl_3$ solution.

CT absorption band. Each photoconduction spectrum is normalized to the light intensity at 360 nm. The resistivity in the dark, and the maximum wavelengths of the photoconduction and the absorption are summarized in Table 2. A large photoconduction peak was observed in all CT salts in the long wavelength side of the CT absorption band (Fig. 4 and Table 2). In TPP–TCP (Fig. 4a) and TPT–TCP (Fig. 4c), another smaller photoconduction peak was observed at the absorption edge of the LE band of the cation. However, it was not seen clearly in TPP–TCM (Fig. 4b) and TPT–TCM (Fig. 4d), perhaps because it was hidden by the large peak. In TPP–ClO_4 and TPT–ClO_4, in which CT interaction is absent between the cation and the anion, only the small peak was found. This indicates that the large photoconduction peak is due to the excitation at the CT band, and the small one to the local excitation of the cation. A relatively small photocurrent was observed when a CT salt was illuminated with a light in the near IR region (800—1100 nm). This may be due to the presence of the deep traps of charge carriers. The spectral dependence curve was reproducible in repeated measurements, and did not depend on the sample of single crystals. The effect of air on the photoconduction spectra was very small.

A typical time response curve of the photocurrent is given in Fig. 5 for TPT–TCP salt. Upon excitation in the CT band (650 nm), the photocurrent increased immediately and rapidly reached a steady state value. When the excitation was removed, the photocurrent decayed rapidly with a considerably long tail, approaching the initial value of the dark current. This suggests that the photoconduction by CT excitation is not strongly limited by charge carrier traps, although shallow traps are present in the crystal. The excita-

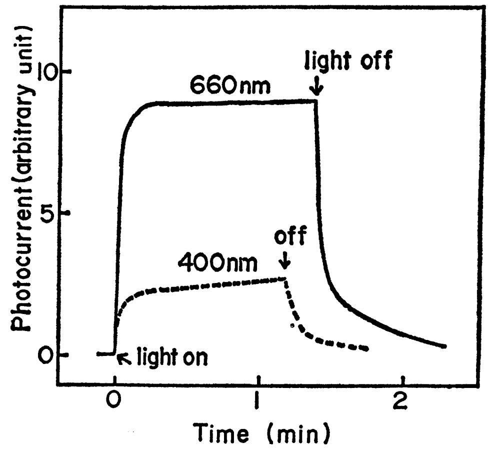

Fig. 5. Time response curves of photocurrent of TPT–TCP salt in vacuum at room temperature.

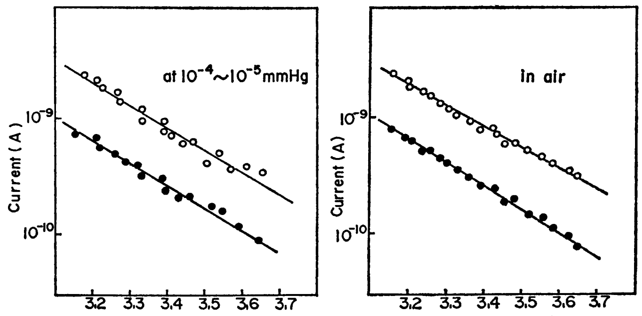

Fig. 6. Temperature dependence of dark current and photocurrent at 650 nm of TPT–TCP salt in vacuum and in air.
—●— dark current, —○— photocurrent.

Table 3. Activation energies of dark and photoconductivities of organic CT salts

Salts	E_{ad} (eV) in vacuum	E_{ad} (eV) in air	E_{aph} (eV) in vacuum	E_{aph} (eV) in air	λ_{ex} a) (nm)
TPP-TCP	0.6	0.5	0.6	0.6	600
			0.6	0.5	1000
TPT-TCP	0.4	0.4	0.45	0.4	650
			0.5	0.5	1000
TPT-TCM	0.9	0.8	0.8	0.7	600
ADPP-TCP	—	0.45	—	0.45	600
ADPT-TCP	—	0.6	—	0.6	600
ADPP-TCM	—	0.45	—	0.35	600
TPT-ClO$_4$	1.2	0.9	1.2	0.9	500
			1.2	0.9	1000

a) wavelength of illuminating light.

tion at 450 nm caused a slightly slower response of the photocurrent.

The temperature dependence of the dark conduction and photoconduction was investigated between 273—323 K. Both for dark- and photocurrents, $i=i_0\exp(-E_a/kT)$ holds. A typical result is given in Fig. 6 for TPT–TCP salt both in vacuum and in air. The activation energy E_a of the photocurrent, 0.45 eV in vacuum and 0.4 eV in air, is approximately the same as that of the dark current, 0.4 eV both in vacuum and in air. The photocurrent at 1000 nm had also essentially the same activation energy 0.5 eV as the photocurrent at 650 nm. The other salts gave essentially the same results (Table 3).

ESR Absorption. A weak ESR signal observed initially in perchlorate salts of TPP and TPT cations disappeared by recrystallization of the salts. Therefore, all CT salts were prepared carefully from the corresponding perchlorate salt which gave no ESR signal. Even when prepared in this way, CT salts showed a single broad ESR absorption band which showed no marked change by further recrystallizations. This indicates that the absorption is not due to impurities. As an illustration, the ESR signal of TPT–TCP salt is given in Fig. 7. The g-values and the total spin concentrations of the CT salts are listed in Table 4. As the value of spin concentration changed to some extent with the crystal, average values are listed. The total spin concentrations 10^{15}—10^{16} spins/gram are much smaller than those observed in many strong molecular CT complexes,[9,10] and almost the same as those measured in weak molecular complexes.[11] These ESR signals seem to arise from the defects in the crystal. Upon illumination with a visible light, intensity of an ESR signal increased slightly but the g-value showed no shift (Fig. 7). The ratio of the ESR intensity on excitation with a white light to that in the dark is listed in Table 4. No ESR absorption was observed when the perchlorate salts of the cation and

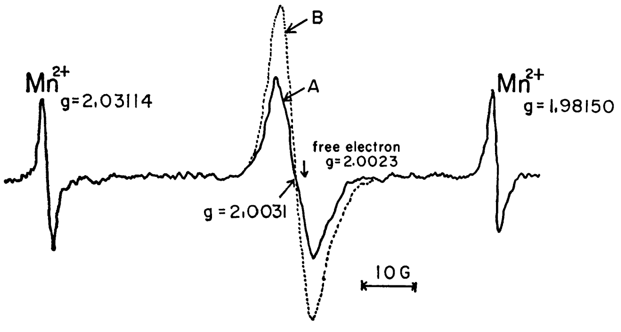

Fig. 7. ESR absorption spectra of TPT–TCP salt in vacuum at room temperature.
—— in the dark, ---- on illumination with a white light.

Table 4. g-Values, total spin concentration ([S]) and the ratio (R) of ESR intensity on illumination with a white light to that in the dark of organic CT salts

Salts	g-Value	[S] (spins/gram)	R
TPP-TCP	2.00270	1×10^{15}	1.3
TPT-TCP	2.00310	2×10^{15}	1.8
TPP-TCM	2.00295	1×10^{16}	1.3
TPT-TCM	2.00380	5×10^{15}	1.4
ADPT-TCP	2.00530	2×10^{15}	1.5
ADPP-TCM	2.00480	1×10^{15}	1.35

alkali metal salts of the anion were irradiated. The lights in the CT band region and in the near IR region (500—1200 nm) were effective on increasing the ESR signal, while those of shorter than 450 nm were ineffective.

The photoresponse curve of an ESR signal of TPT–TCP salt is given as an example, in Fig. 8. The curve at room temperature showed a fairly rapid rise and decay, and was similar to that of the photocurrent shown in Fig. 5. No significant difference in ESR absorption was found between that in vacuum and in air. The spectral response, time response and the effect of air of the photo-ESR absorption suggest a close relationship between the photo-induced paramagnetism and the photoconduction of the CT salts.

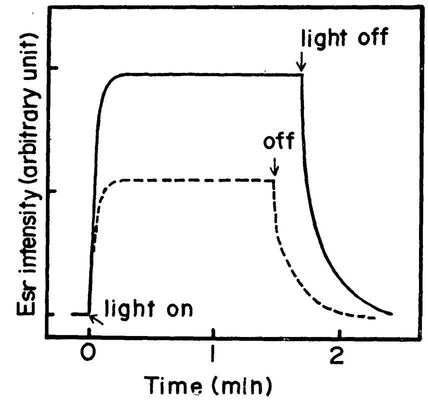

Fig. 8. Time response curves of photo-ESR absorption of TPT-TCP salt in vacuum at room temperature. —— on illumination at 500—1200 nm, ---- on illumination at 500—700 nm.

The temperature dependence of an ESR absorption in the dark and on irradiation was investigated in the range 213—323 K. The total spin concentration and the g-value of an ESR signal in the dark showed no significant change when temperature was lowered, indicating that the amount and nature of the paramagnetic species which existed originally in the material are independent of the temperature. The photo-ESR absorption showed a gradual decrease in its spin concentration with the decrease of temperature, activation energy being slightly negative (<0.2 eV). Thus, both the paramagnetic species induced by light and those originally present in the crystal in the dark are not produced by the thermal activation process.

Discussion

General Feature of the Electrical Conduction. (i) *All CT salts show a larger photoconduction peak at the long wavelength side of the interionic CT absorption band, and the photoconduction is almost unaffected by the presence of air*: This photoconduction is much larger than that observed in the perchlorate salt of the corresponding cation. A good reproducibility of the photoconduction was observed during the course of repeated measurements. Even when measured on different single crystals, the behavior of the photoconduction remained almost unchanged. This suggests that the observed conduction in this region is intrinsic and the photoexcitation of the interionic CT band contributes to the photoconduction.

Charge carriers seem to be generated in the bulk rather than on the surface of a crystal. Carrier generation in the bulk can account for the CT absorption peak not coinciding with the photocurrent peak; the number of photons reaching the bulk of a crystal are larger at the edge of the absorption band than at the absorption peak. The photocurrent, which is insensitive to the presence of air, also supports bulk carrier generation.

(ii) *All CT salts show a smaller photoconduction in the near IR region of 800—1100 nm, which is also insensitive to the presence of air*: This suggests the presence of deep traps at 1.0—1.4 eV below the conduction level. As the value is considerably larger than the observed activation energy, the dark current cannot be caused by the thermally activated carrier generation from these deep traps.

(iii) *When excited in a LE band of the cation, the photoconduction does not appear significantly*: This may be due to the fact that the photon is absorbed mostly on the surface of a crystal. However, the photon in the absorption edge of the LE band can reach the bulk of a crystal, and produce the photocarrier as in the case of CT band excitation as follows,

$$\begin{array}{ccccccc} (D^-A^+) & \xrightarrow{h\nu} & (D^-A^{+*}) & \longrightarrow & (D\cdot A\cdot)^* & \longrightarrow & (D\cdot + A\cdot) \\ \text{ground state} & & \text{locally excited state} & & \text{excited CT state} & & \text{photocarriers} \end{array}$$

(iv) *The photocurrent in the CT absorption region is proportional to about the 0.5 power of the incident light intensity*: As the photocunduction in this region seems to be intrinsic, one photon absorption produces two charge carriers. However, if the carriers disappear with recombination between electrons and holes during migration, the concentration of the carrier would be proportional to the 0.5 power of the light intensity. Thus the photoconduction in our system may be recombination limited.

(v) *Both dark conductivity and photoconductivity in the CT absorption and near IR regions have the same activation energy*: As can be seen in Table 3, the most striking results obtained for the electrical properties of organic CT salts is that the values of activation energy for dark conduction and photoconduction are the same without any exception with respect to the six CT salts investigated. The property seems to be general with this kind of organic salts, and is basically important for framing up the conduction mechanism in the salts as in the following.

Mechanism of the Electrical Conduction in Organic CT Salts. The property mentioned above reminds us that a "trapping conduction mechanism" is the simplest model for explaining the agreement of the values of the activation energy of dark conduction and photoconduction. The trapping conduction model is shown schematically with TPT–TCP salt in Fig. 9 as an example. The TPT–TCP crystal has trapped carriers 0.4 eV below the conduction level which are thermally

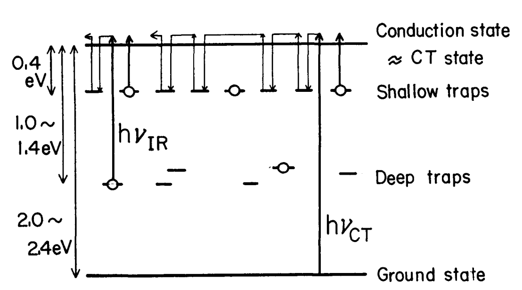

Fig. 9. Trapping conduction model with TPT-TCP salt.

excited up to conduction level in the dark, and the carriers generated in this way migrate through the crystal repeating the trapping and detrapping processes. Thus, the activation energy in dark conduction should be 0.4 eV, the depth of the trap levels below the conduction level, being the energy required for the trapping conduction.

In the case of photoconduction, the photocarriers are spontaneously generated in the conduction level by the absorption of light in the CT band, since the energy level of the conduction state is approximately equal to that of the excited CT state. The photocarriers thus generated migrate by the trapping conduction mechanism. In this mechanism, no activation energy is required for the carrier generation, and the activation energy of 0.4 eV as observed should be consumed in the carrier migration process. Thus, both for dark conduction and photoconduction the same amount, 0.4 eV, of activation energy is required. Photocarriers generated from the deep trap levels by near IR illumination also require the same activation energy 0.4 eV for their migration.

In our present model, only electron carriers are considered. As the molecular size of the acceptor cation is considerably larger than that of the donor anion, the acceptor radical A·, *i.e.*, electron, might contribute predominantly to the photocurrent. Molecular arrangement in the crystal supports this view.[12]

Photoconduction and Paramagnetic Species. An investigation of the ESR of the salts revealed that (a) CT salts showed a temperature independent ESR absorption even in the dark, (b) the perchlorate salts in which CT ineraction is absent gave no ESR signal, (c) the total spin concentration was of the order 10^{15}—10^{16} spins/gram, the amount changing considerably measured on different samples, (d) photo-illumination increased the ESR signal, the photo-ESR absorption showing a similar time response and spectral response with photocurrent, and (e) the temperature dependence of the photo-ESR absorption showed a slightly negative activation energy, the signal increasing with the lowering of temperature, and the time response curve of the phot-ESR absorption showed considerably longer rise and decay at lower temperatures.

The temperature independent ESR signal in the dark may be due to the charge carriers trapped in shallow traps (Fig. 9). These trapped carriers may be generated from crystal defects by CT interaction, because of (b) and (c). Photocarriers and the paramagnetic species of the photo-ESR may be the same (d), as can be seen in Fig. 9. The slightly negative activation energy of the photo-ESR (e) may be understood by the decrease of the recombination of the paramagnetic species with the lowering of temperature. Actually, the time response curve of the photo-ESR absorption shows considerably longer rise and decay at lower temperatures. Since paramagnetic species and the charge carriers are the same, the behavior of the photo-ESR signal is in line with the recombination limited photoconductivity, a photocurrent being proportional to the 0.5 power of the light intensity.

In the case of strong molecular CT complexes, such as perylene-iodine complex, a good coincidence between the values of the activation energy of dark current and of unpaired spin concentration was observed. This was used for proof that the paramagnetic species observed in the ESR spectroscopy were identical with the carriers.[9] This kind of coincidence is not necessary in our system, since the thermal activation process in the dark conduction is the carrier migration process. If the carrier concentration in the dark is equal to the spin concentration, about 10^{15} electrons/gram, the mobility of the carrier is estimated to be 10^{-5}—10^{-6} cm^2/volt·sec from the relation $i=Ne\mu$, where N is carrier concentration, e electric charge and μ mobility. The value seems to be very small as compared with the observed mobilities of organic compounds.[13] However, taking account of the fact that a fairly large energy is required for the carrier migration, and that the photoconduction is recombination limited, this small value of mobility is conceivable.

Another Mechanism of the Electrical Conduction. Although the above mechanism can account for the results of the electrical and magnetic properties of the organic CT salts, it should be noted that other mechanisms are possible for both carrier generation and migration. At first, charge carriers can be generated by the interaction between crystal imperfections and CT excitons migrating in a crystal. In this case, the carrier generation is extrinsic. This mechanism is the same as that suggested by Akamatu and Kuroda for the photoconduction of pyrene complexes.[3] Both mechanisms can explain the spectral, temperature and light intensity dependences of the photocurrent, but from the fact that the behavior of the photoconduction shows a good reproducibility when measured on several samples of single crystals, we consider the former mechanism, that is, the intrinsic carrier generation, to be plausible.

With weak molecular CT complexes, Akamatu and Kuroda suggested that the energy equivalent to the difference of the energy between the conduction level and the CT exciton level is required for the separation of a D^+A^- ion-radical pair. In this case, CT excitons cannot be separated spontaneously into charge carriers. However, in interionic CT salts, the interaction between two neutral radical species, D·A·, in the excited CT state may be small and consequently an energy required for the charge separation is smaller than that in the case of molecular CT complexes, and the photocarriers can be generated from the excited CT state with a very small thermal energy compared with the activation energy for the migration. Thus, the energy level of the conduction state can be approximately equal to that of the excited CT state, and the intrinsic charge carrier generation seems to be possible in organic CT salts.

A hopping mechanism may be possible for the carrier migration process, instead of the trapping conduction. In this case, the charge carrier migrates from an ion to another with an activation energy 0.4—0.8 eV. This value seems to be fairly large for the activation energy for hopping conduction. However, these two mechanisms, *i.e.*, trapping conduction and hopping conduction, can explain the experimental results, and the latter possibility cannot be excluded.

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