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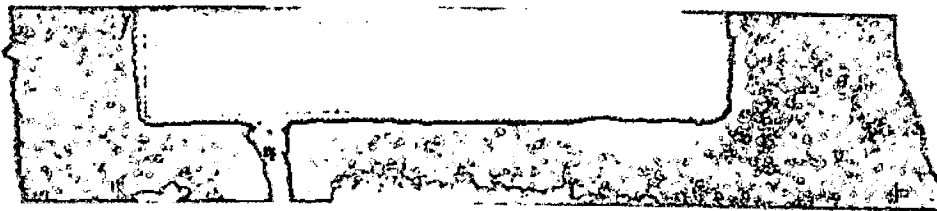# UNIVERSITY OF CALIFORNIA

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II. EFFECTS OF ADDED ELECTRON ACCEPTOR ON METAL-FREE PHTHALOCYANINE

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Abstract

The addition of ortho-chloranil to the surface of films of metal-free phthalocyanine has been found (a) to increase the dark conductivity of such films by as much as 10^7, (b) to increase the steady-state photoconductivity by as much as 10^5, and (c) to result in the formation of unpaired electrons whose concentration decreases reversibly as a result of illumination. These systems exhibit a light-induced polarization, the phthalocyanine layer becoming more positive with respect to the ortho-chloranil layer. Kinetic studies demonstrate that, upon illumination, a single process (time constant = 40 seconds) results in the increase in conductivity, the decrease in unpaired spins, and the increase in polarization. The results are consistent with the following scheme. An electron transfer from phthalocyanine to ortho-chloranil occurs in the dark at room temperature, producing holes in the phthalocyanine layer and ortho-chloranil negative ion radicals (high conductivity, ESR signal). Illumination results in the transfer of an electron from an excited phthalocyanine molecule to the ortho-chloranil negative ion, producing further phthalocyanine holes and ortho-chloranil double-negative ion (increase in conductivity, increase in polarization, decrease in ESR signal). By equating spin concentration with charge-carrier concentration (phthalocyanine holes) it is possible to calculate a mobility of 10^{-4} cm^2/volt/sec for holes in the phthalocyanine layer. By use of this value, a quantum yield of unity is calculated for the production of charge carriers in doped phthalocyanine. The experiments indicate a quantum yield of less than 10^{-1} for undoped phthalocyanine. The over-all results of adding a strong electron acceptor to a film of phthalocyanine are thus to (a) produce charge carriers in the dark, (b) increase the quantum yield for production of charge carriers by light, and (c) increase charge-carrier lifetime.

ELECTRICAL PROPERTIES OF ORGANIC SOLIDS.
II. EFFECTS OF ADDED ELECTRON ACCEPTOR ON METAL-FREE PHTHALOCYANINE[*][†]

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Introduction

A number of studies have indicated that the conductivity of organic semiconductors may be significantly altered by the presence of impurity materials. For example, gases such as O_2, Cl_2, and NO_2 have been found to increase both the semiconductivity and photoconductivity of anthracene crystals by several orders of magnitude.[1,2] Similar effects have been observed with O_2 and metal-phthalocyanines.[3] Akamatu et al.[4,5] have studied complexes between halogens and polycyclic aromatic compounds and have found 10^7-10^9-fold increases in dark conductivity over that of the pure hydrocarbon. All the above effects have been tentatively interpreted by the respective authors as due to an increase in the mobility of charge carriers[1,2,3,6,7] caused by interaction bwtween the impurity and the host molecules.

The results quoted above suggest that there may be a general effect of oxidizing agents (electron acceptors) upon the conductivity properties of certain organic substances (donors). Therefore we felt it to be of interest to investigate the effects of organic oxidizing agents upon such properties.

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[1]W.G. Schneider and T.C. Waddington, J. Chem. Phys. 25, 358 (1956).

[2]D.M.J. Compton and T.C. Waddington, J. Chem. Phys. 25, 1075 (1956).

[3]A.T. Vartanyan and I.A. Karpovich, Dokl. Akad. Nauk S.S.S.R. 111, 561 (1956).

[4]H. Akamatu, H. Inokuchi and Y. Matsunaga, Bull. Chem. Soc. Japan 29, 213 (1956).

[5]H. Akamatu and H. Inokuchi, in Proceedings of the Third Conference on Carbon (Pergamon Press, New York, 1959), p. 51.

[6]Akamatu, Inokuchi, and Matsunaga, Bull. Chem. Soc. Japan 29, 213 (1956); see p. 218.

[7]Lyons, Bree, and Morris, in Proceedings of the Third Conference on Carbon (Pergamon Press, New York, 1959), p. 87.

Further interest in this problem is generated by the fact that aggregates of porphyrin molecules (chlorophyll) and organic oxidizing agents (quinones, coenzyme Q,[8] etc.) , as well as reducing agents (carotenoids),[9,10] occur together in photosynthetic materials, and their interaction may be of importance in the primary quantum conversion process.

High conductivities have been observed in chloranil, iodanil, and bromanil complexes of dimethylaniline;[11] electron spin resonance (ESR) has been observed in molecular compounds of diamines and substituted benzoquinones.[12] Previous work from this laboratory has demonstrated that one can achieve large increases in dark conductivity of metal-free phthalocyanine upon the addition of small amounts of ortho-chloranil.[13] In addition, a qualitative parallelism between the ESR signal and the conductivity of various phthalocyanine samples was observed.[14] The studies presented herein represent an extension of this work.

Experimental Procedure

The principal organic semiconductor used in these studies was phthalocyanine, although additional experiments were carried out with tetracene, coronene, and decacyclene. Methods of sample preparation and conductivity measurements were as described previously.[15] The oxidizing agents were applied by spraying a benzene solution onto the exposed area of a surface cell[15] of the organic semiconductor. Occasional samples were prepared from solutions containing both donor and acceptor molecules, but results from such samples require further investigation.

Electron spin resonance measurements were carried out with a previously described spectrometer.[16]

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[8] F. L. Crane, Plant Physiol. **34**, 128 (1959).

[9] Blass, Anderson, and Calvin, Plant Physiol. (in press).

[10] Sapozhnikov, Kayasovskaya, and Maevskaya, Dokl. Akad. Nauk S.S.S.R. **113**, 74 (1957).

[11] D. D. Eley and H. Inokuchi, in Proceedings of the Third Conference on Carbon (Pergamon Press, New York, 1959), p. 91.

[12] Bijl, Kainer, and Rose-Innes, J. Chem. Phys. **30**, 765 (1959).

[13] D. Kearns and M. Calvin, in Bio-Organic Chemistry Quarterly Report, UCRL-8457, Sept. 1958, p. 25.

[14] D. R. Kearns and M. Calvin, unpublished results.

[15] G. Tollin, D. R. Kearns, and M. Calvin, Electrical Properties of Organic Solids. I. Kinetics and Mechanism of Conductivity of Metal-Free Phthalocyanine, UCRL-8843, July 1959.

[16] Sogo, Pon, and Calvin, Proc. Natl. Acad. Sci. U.S. **43**, 387 (1957).

Results

In a series of preliminary experiments, it was found that the dark conductivity and photoconductivity of phthalocyanine, tetracene, decacyclene, and coronene were increased to varying degrees by the addition of small amounts of either ortho-chloranil, chloranil, or phenanthrene-quinone. Inasmuch as the largest effects were obtained with ortho-chloranil— phthalocyanine mixtures, it was decided to limit this investigation to this system.

Dark Conductivity

The variation of the room-temperature dark conductivity of a phthalocyanine sample with the amount of added ortho-chloranil is shown in Fig. 1. It is apparent that the dark conductivity increases with increasing amounts of ortho-chloranil (doping) to a maximum value of about 10^7 times that of the pure phthalocyanine.

A decrease in temperature from $25^\circ C$ to $-100^\circ C$ resulted in a decrease in the dark conductivity of a heavily doped phthalocyanine sample by a factor of about 10^3. This corresponds to an activation energy of approximately 0.2 ev.

Steady-state Photoconductivity

The variation of the room-temperature steady-state photoconductivity or ortho-chloranil-doped phthalocyanine with ortho-chloranil concentration is also shown in Fig. 1. The maximum photocurrent obtained with a heavily doped sample was about 10^5 times that obtained with undoped material.

A decrease in temperature from $25^\circ C$ to $-100^\circ C$ resulted in a decrease in the photoconducitivity of a heavily doped phthalocyanine sample by a factor of about 4×10^2. This again corresponds to approximately a 0.2-ev activation energy. [17]

A summary of the above results is given in Table I.

The spectral response of photoconductivity in a lightly doped sample follows the absorption spectrum of pure phthalocyanine. As the amount of doping increases, however, a photoinduced decrease in conductivity can be observed at certain wave lengths. The magnitude of this effect increases with increasing doping but is never more than a few percent of the photo- induced increase in conductivity produced by phthalocyanine absorption. The spectral response of this effect is shown in Fig. 2. The significance

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[17] Because of the experimental difficulties involved in measuring the temperature dependence of dark conductivity in cells of the type used in these experiments (see Reference 15), it is not certain that the slightly larger decrease in dark conductivity upon cooling is significant.
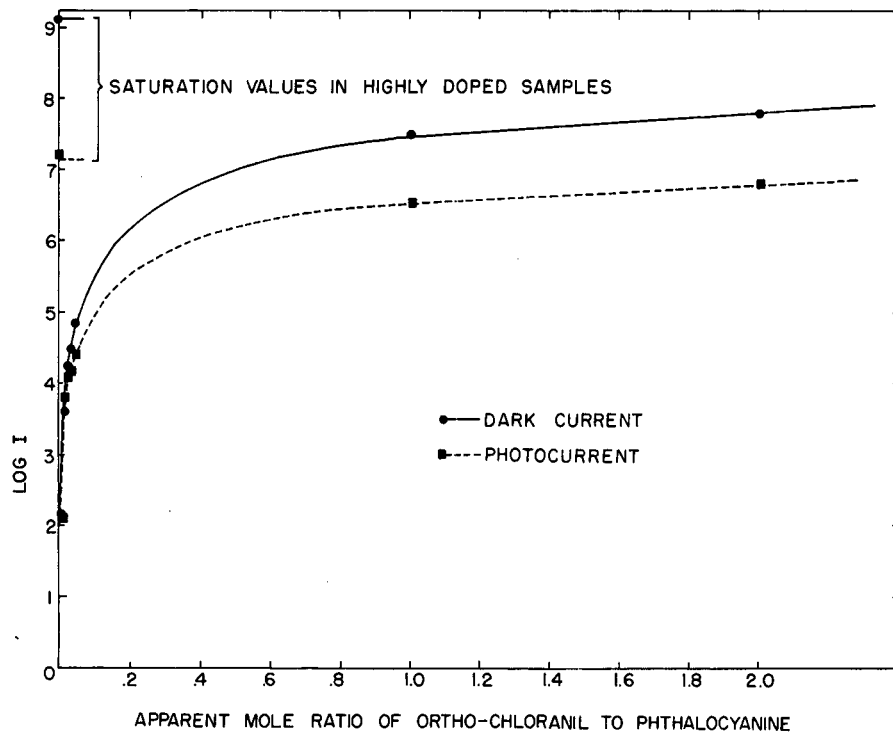
Fig. 1. Variation of dark conductivity and photoconductivity
   of phthalocyanine with amount of ortho-chloranil added.

Table I

Comparison of the maximum values of the conductivity of ortho-chloranil-doped metal-free phthalocyanine with the conductivity of pure metal-free phthalocyanine. The room-temperature specific resistivity of pure metal-free phthalocyanine was approximately 10^9 ohm cm, and that for the doped material was approximately 10^2 ohm cm. The units in the table are relative to the value for pure phthalocyanine at $-100°C$.

Temperature	Undoped		Doped		Doped/Undoped	
	Dark cond.	Steady-state photoconductivity	Dark cond.	Steady-state photoconductivity	Dark cond.	Steady-state photoconductivity
25°C	10^3	10^3	10^{10}	10^8	10^7	10^5
-100°C	10^{-7}	1	10^7	2.5×10^5	10^{14}	2.5×10^5
25°C/-100°C	10^{10}	10^3	10^3	4×10^2	--	--

ACTION   SPECTRUM   OF   THE   REVERSE
PHOTOCONDUCTIVITY   EFFECT   (100 Å BANDWIDTH)

THE   SPECTRUM   WAS   MEASURED   UNDER   THE   CONDITION
OF   CONSTANT   ENERGY   AT   ALL   WAVELENGTHS
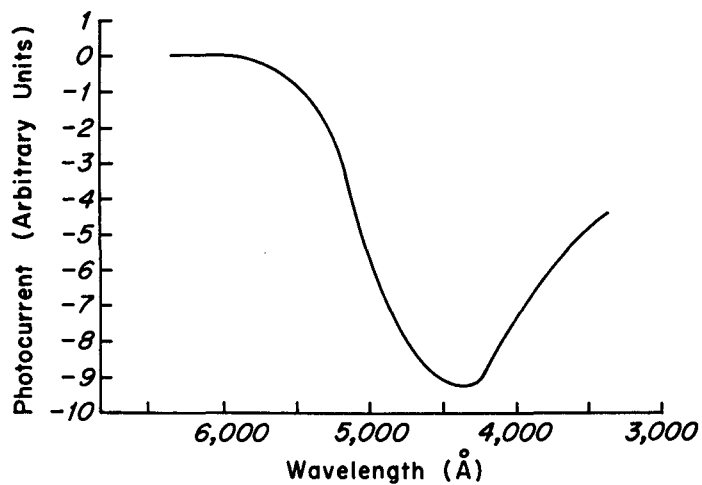
MU—17528

Fig. 2.   Action spectrum of the reverse photoconductivity
effect (100 Å bandwidth).   The spectrum was measured
under the condition of constant energy at all wave lengths,
and at a scanning rate of approximately 100 A°/3 sec.

of this action spectrum is not unambiguous inasmuch as it represents the
resultant of two opposing processes. Cooling the sample causes this
effect to disappear, with the result that wave lengths which produced a
decrease in conductivity at room temperature produce an increase in
conductivity at the low temperatures. It is also possible to observe the
replacement of the decrease at room temperature by an increase in photo-
conductivity if the illumination at that wave length is prolonged.

The rise and decay curves for photoconductivity induced in ortho-
chloranil-doped phthalocyanine by light in the phthalocyanine absorption
bands consist of two components. One of these is quite rapid and has time
constants essentially the same as those of the undoped material. The other
component is very much slower and is unimolecular for both rise and decay,
with a time constant of about 40 seconds. This is shown for the photo-
conductivity decay in Fig. 3. The fact that rise time equals decay time
requires that the process be determined by the balance of the rate of input
of quanta and the intrinsic decay rate, $\frac{dX}{dt} = (const) I_0 - \lambda X$, where I_0
is the rate of input of quanta and λ is the unimolecular decay constant. The
ratio of slow to fast components increases with increasing doping. In the
most heavily doped samples, the photoconductivity rise and decay can be
attributed almost, entirely to the process with the 40-second time constant.
At low temperatures, the time constant decreases and is about 25 seconds
at $-100^\circ C$.

Electron Spin Resonance

It was observed that when ortho-chloranil was added to a sample of
phthalocyanine in the manner described above, a large ESR absorption could
be detected, corresponding to the presence of unpaired electron spins in the
sample (see Fig. 4). The greater the extent of doping, the greater the ESR
signal. When the sample was cooled to about $100^\circ C$ in the spectrometer
cavity, no change in spin concentration or line shape could be observed.

As it was not possible to achieve uniform mixing of phthalocyanine and
ortho-chloranil, it was therefore not possible to measure the ratio of unpaired
spins to the number of ortho-chloranil molecules in actual contact with
phthalocyanine molecules. The number (by comparison with diphenylpicryl-
hydrazyl) of unpaired spins per total number of ortho-chloranil molecules
added is 0.01. It is of interest to note that even in those cases for which
stoichiometric compounds between electron donor (reductant) and electron
acceptor (oxidant) have been measured, the number of unpaired electron spins
is always much smaller than that expected for simple complete electron transfer
complexes ($[D \cdot]^{\oplus} [A \cdot]^{\ominus}$).[18,19]

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[18] Y. Matsunaga, J. Chem. Phys. $\underline{30}$, 855 (1959).

[19] Buck, Lupinski, and Oosterhoff, Mol. Phys. $\underline{1}$, 196 (1958), and private
communication
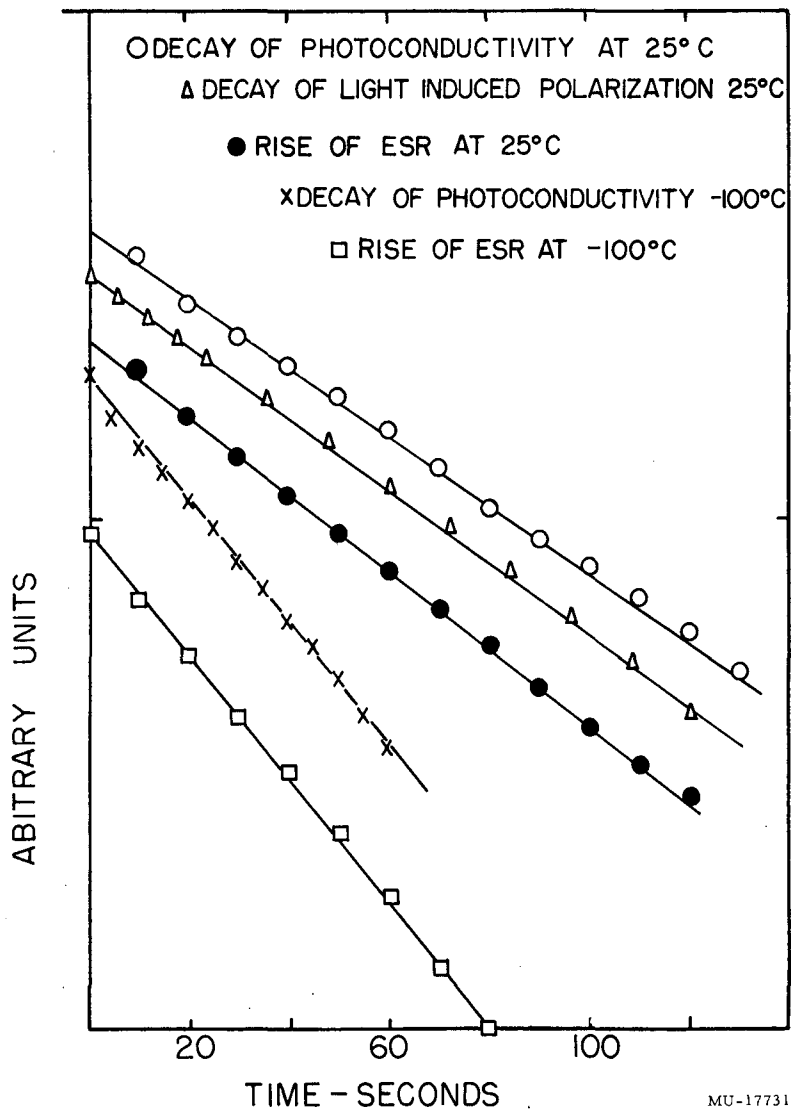
Fig. 3. Semilog plots of time dependence of photoconductivity, light-induced ESR, and light-induced polarization in doped phthalocyanine. The relative positions of each of the curves in this figure are not comparable.

ELECTRON SPIN RESONANCE SPECTRUM OF

O-CHLORANIL "DOPED" METAL FREE PHTHALOCYANINE

|← ∼ 5 gauss →|
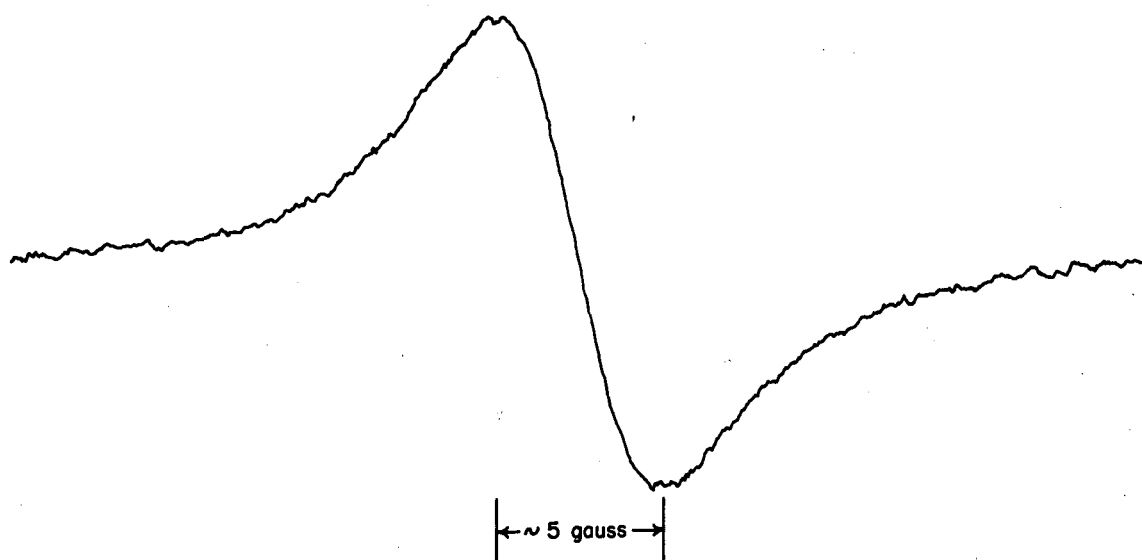
MU-17527

Fig. 4. Electron-spin-resonance spectrum of ortho-chloranil-
         doped phthalocyanine. The curve represents the first
         derivative of the absorption.

When a heavily doped sample was illuminated in the ESR spectrometer, a decrease in unpaired spins could be observed (Fig. 5). The magnitude of this effect corresponded to a decrease of approximately 5 to 20% in the spin concentration, depending upon the sample used, and was independent of the temperature. The spectral response of the photodecrease in spin concentration followed the phthalocyanine absorption spectrum. The photoinduced decrease in ESR and the subsequent rise in spin concentration, when the light was turned off, followed unimolecular kinetics, with a time constant of approximately 40 seconds (Fig. 3). At -100°C, the time constant decreased to about 25 seconds (Fig. 3).

Light-Induced Polarization

When an ortho-chloranil-doped phthalocyanine film was placed between the plates of a condenser, a charging of the condenser could be observed by using a vibrating-reed electrometer to measure the voltage developed (Fig. 6). The sign of the induced charge on the condenser plates indicated that the phthalocyanine layer was positive with respect to the ortho-chloranil. When such a cell was illuminated, an increase in polarization was observed. The spectral response of the photoinduced charge produced on the plates corresponded to phthalocyanine absorption. The polarity of the effect demonstrated that upon illumination the phthalocyanine layer became more positive with respect to the ortho-chloranil layer.

The rise and decay of the light-induced charge on the condenser plates followed unimolecular kinetics with a room-temperature time constant of about 40 seconds (Fig. 3). The experimental arrangement did not permit cooling of the sample.

Flash-Induced Photoconductivity

A moderately doped sample of phthalocyanine was examined by the flashing-light method described previously.[15] The decay of the photoconductivity produced by light in the phthalocyanine absorption region is shown in Fig. 7, together with a decay curve for undoped material with and without ambient illumination.[15]

Discussion and Conclusions

The concurrent increase in dark conductivity and ESR in phthalocyanine upon the addition of ortho-chloranil may be explained in the following manner. Ortho-chloranil is a strong oxidizing agent and therefore might be expected to remove electrons from the phthalocyanine if the two substances were placed in intimate contact. The relative ease of transfer of electrons from the phthalocyanine to the ortho-chloranil would depend upon the electron affinity of ortho-chloranil and the ionization potential of phthalocyanine. It is postulated, then, that such an electron transfer takes place in the dark in the doped samples. This gives rise to the observed ESR. Positive holes which can conduct are formed in the phthalocyanine layer as a result of the transfer and give rise to the large dark currents. This electron-transfer

EFFECT OF ILLUMINATION ON THE ELECTRON SPIN RESONANCE SIGNAL OF

O-CHLORANIL "DOPED" METAL FREE PHTHALOCYANINE

CURVE REPRESENTS UNPAIRED SPIN CONCENTRATION VS. TIME

Light on

SPIN CONCENTRATION

Light off

|←1 Min→|
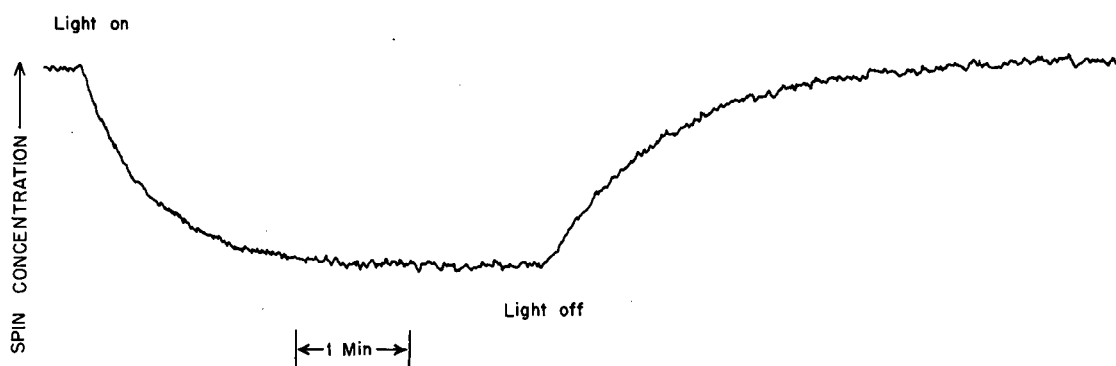
MU-17529

Fig. 5. Effect of illumination with white light on the ESR
signal in ortho-chloranil-doped phthalocyanine. Curve
represents unpaired spin concentration vs time.

TRANSPARENT
CONDUCTORS

PHTHALOCYANINE   ORTHO-CHLORANIL

VIBRATING REED
ELECTROMETER
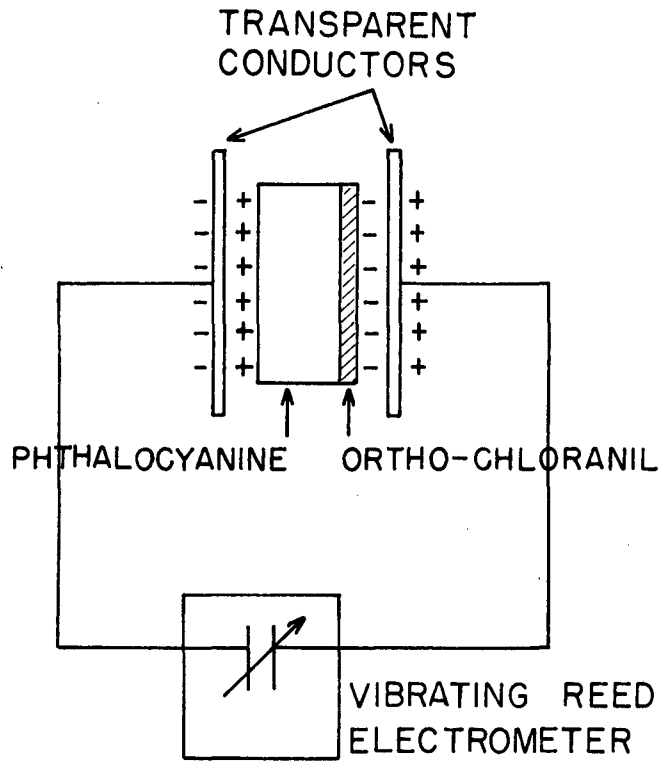
MU-17730

Fig. 6. Schematic diagram of polarization apparatus. The
   plates of the condenser were approximately 10^{-2} cm
   apart. The maximum voltage obtainable in this system
   upon illumination was about 100 mv.
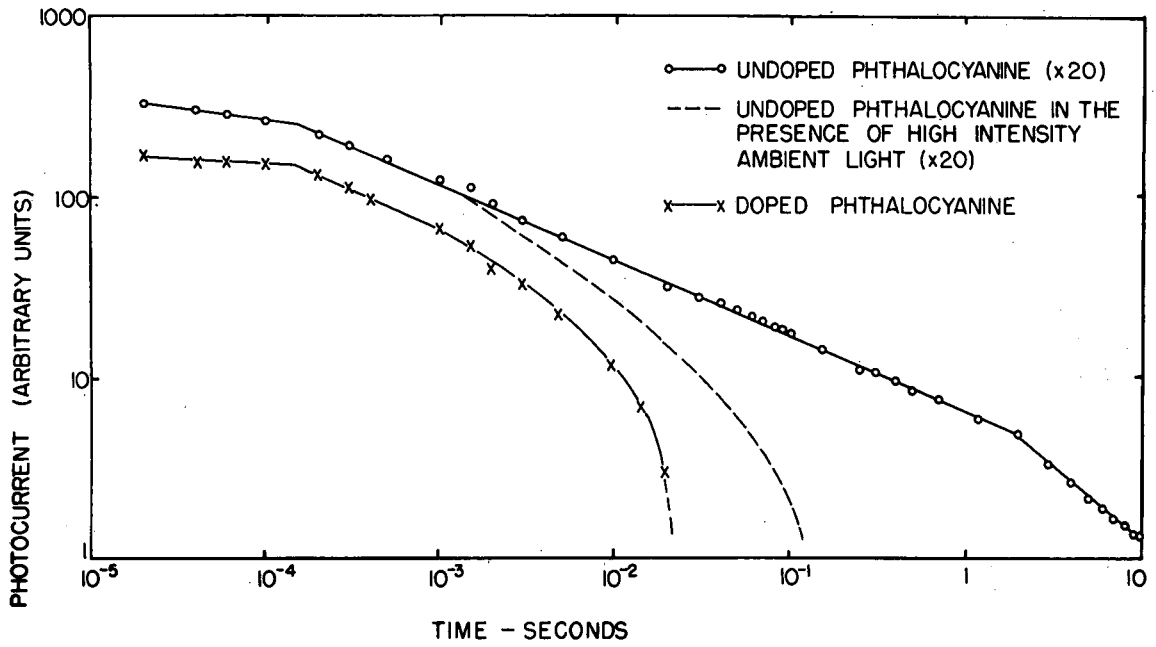
MU - 17732

Fig. 7. Flash-induced photoconductivity in doped phthalocyanine
compared with that in undoped phthalocyanine with and
without ambient illumination.

process may be represented by the equation[20]

$$PH + CH \rightarrow PH^{\oplus} + CH^{\ominus} . \tag{1}$$

The dark polarization of the ortho-chloranil–phthalocyanine system is consistent with Reaction (1). Ortho-chloranil negative ions would not be expected to significantly contribute to the conductivity because they are separated from the electrodes by a relatively thick phthalocyanine layer.

The mechanism proposed in Reaction (1) postulates that the increase in dark conductivity upon doping is due to the actual formation of charge carriers, rather than an increase in the mobility of charge carriers already present in the undoped material. This is supported by the following observations: (a) The dark conductivity of pure phthalocyanine has an activation energy of about 1 ev.[15] This has been ascribed primarily to the process of formation of charge carriers.[21] On the other hand, the photo-conductivity of pure phthalocyanine has an activation energy of only 0.2 ev,[15] and this can be interpreted in terms of charge-carrier mobility.[22] The fact that cooling a doped phthalocyanine sample to -100°C does not decrease the ESR signal and produces a much smaller decrease in dark conductivity (Table I) than is produced in an undoped sample demonstrates that the primary process which occurs in the dark upon doping is not appreciably reversed at the low temperature. Therefore, the decrease in dark conductivity in doped material at -100°C can be attributed to the temperature dependence of mobility. Such an identification is supported by the fact that photoconductivity in both doped and undoped samples has this same temperature dependence. This, we feel, is strong evidence that the main result of doping is to produce charge carriers. (b) When moderately doped samples are subjected to flash illumination the decay curves for photoconductivity are essentailly identical with the curves obtained with undoped samples in the presence of high-intensity ambient illumination (Fig. 7).[15] This indicates that charge carriers are indeed produced by doping and that these carriers behave in the same manner as do photo-produced carriers.

[20]The following abbreviations are used in the discussion:

PH = metal-free phthalocyanine
CH = ortho-chloranil
PH* = first excited singlet state of phthalocyanine
PH$^{\oplus}$ = phthalocyanine holes
CH$^{\ominus}$ = ortho-chloranil negative-ion radical
CH$^{\ominus}$ = ortho-chloranil double-negative ion

[21]C. G. B. Garrett in *Semiconductors*, Ed. by N. B. Hannay, (Rheinold, New York, 1959), Chap. 15, p. 662 ff.

[22]Kommandeur, Korinek, and Schneider, Can. J. Chem. **35**, 998 (1957).

        Although the above results definitely indicate that the increased dark
conductivity in doped samples is primarily the result of an increased charge-
carrier concentration, it is not possible to completely eliminate a small
effect upon the charge-carrier mobility (see below).

        The spectral responses of the photoconductivity and of the light-
induced decrease in ESR, and the time constants for the rise of photo-
conductivity and for the light-induced decrease in ESR, indicate that the
same process gives rise to photoconductivity and results in a decrease in
the concentration of unpaired spins. This may be accounted for by the
following processes:

$$PH + h\nu \rightarrow PH^*, \tag{2}$$

$$PH^* + CH^{\ominus} \rightarrow PH^{\oplus} + CH^{\ominus}. \tag{3}$$
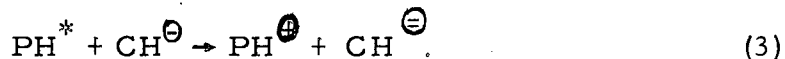
This requires that the paramagnetic species observed in ESR be $CH^{\ominus}$
and that $PH^{\oplus}$, although paramagnetic, is not detected, perhaps because of
broadening of the resonance line. The decrease in ESR, then, is the result
of the transformation of $CH^{\ominus}$ radicals into $CH^{\ominus}$ ions which, owing to
aromatization of the pi-electron system, would not be paramagnetic. The
40-second time constant observed in these experiments demonstrates that
charge carriers have a considerably longer lifetime in the doped material
than in the undoped material. This would result in a large increase in
steady-state photoconductivity upon doping, in agreement with experiments.

        It is also possible to interpret the light-induced polarization
phenomenon in terms of Reaction (3). It is apparent from the method of
doping and from Fig. 6 that most of the $CH^{\ominus}$ radicals will be in fixed
positions near one surface of the phthalocyanine layer. Therefore the
postulated electron transfer from PH^* to $CH^{\ominus}$ should result in an increased
polarization, in which the ortho-chloranil layer becomes more negative
with respect to phthalocyanine. The rise time, spectral response, and
measured polarity of the polarization effect are consistent with this hypothesis.

        It was noted above that the decay of photoconductivity, the rise of
ESR, and the polarization decay after illumination ceased were all unimolecular
processes having the same time constant. This can be interpreted in terms
of the following reaction as the rate-limiting step in all these processes:

$$PH^{\oplus} + CH^{\ominus} \rightarrow PH + CH^{\ominus}. \tag{4}$$
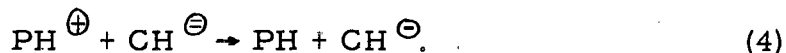
Inasmuch as the concentration of $PH^{\oplus}$ is high in the dark and is not appreciably
changed by illumination (Table I), Reaction (4) should result in pseudo-
unimolecular kinetics. Since this reaction is relatively slow (40-second time
constant) and yet has only a negligible apparent activation energy, there must
be some intrinsic improbability in it, as yet not understood. It is also not
possible at present to account for the decrease in time constant at low
temperatures.

It is conceibable that the energy relationships between the species mentioned above are such as to allow a thermally induced electron transfer from PH to CH $^\ominus$, resulting in the presence of a small amount of CH $^\ominus$ in the dark at room temperature. It is therefore possible to interpret the photoinduced decrease in conductivity (Fig. 2) as the result of an excitation of CH $^\ominus$ and the subsequent transfer of an electron to PH $^\oplus$, forming PH and CH $^\ominus$. At -100°C the amount of CH $^\ominus$ becomes vanishingly small, resulting in the disappearance of this photoreversal. The wave length for maximum response at 4300 Å (Fig. 2) might very well correspond to the absorption of CH $^\ominus$ in the matrix in which it finds itself.

According to Reaction (1), the number of unpaired spins produced by doping (neglecting the CH $^=$ concentration) is a measure of the number of charge carriers produced in the phthalocyanine layer. Thus, by measuring the conductivity of a sample with a measured spin concentration, one can calculate a charge-carrier mobility by the equation

$$I = \mu \, N \, E \, A, \tag{5}$$

where I = current in electrons per second,
    μ = mobility in cm^2 per volt per second,
    N = number of charge carriers per cm^3,
    E = field strength,
    A = cross-sectional area of conductor.
Such a calculation results in a value of 10^{-4} cm^2/v/sec for the mobility of holes in ortho-chloranil-doped phthalocyanine. By measuring the number of light quanta required to produce a given current,[23] it is possible to calculate a quantum yield for the production of holes in such a system, using the above value for the mobility. This was found to be approximately unity.

It is interesting to compare the mobility given above with those obtained in inorganic semiconductors such as germanium and silicon. These latter normally range from 1 to 1000 cm^2/v/sec at room temperature. Therefore, a value of 10^{-4} cm^2/v/sec for an organic material is in keeping with the large differences between the crystal interactions in valence crystals and those in organic molecular crystals. For example, heats of sublimation are about 3 to 4 ev for valence crystals and about 10^2 ev for molecular crystals.

It is of interest to inquire into the relationship between charge carriers in doped and undoped phthalocyanine. It was noted above that the behavior of the flash-induced photoconductivity of doped phthalocyanine was essentially identical with that of pure phthalocyanine in the presence of high-intensity ambient light. This would argue that the dark carriers and the light-produced carriers in doped material are the same as those produced by light in undoped material, that is, in both cases current is carried by holes in the phthalocyanine layer.

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[23] The quantum yield was determined by measureing the ratio of the initial rate of rise of photoconductivity to the rate of input of quanta. The measurement was carried out over a time interval of 1 second. The fact that the time constant for photocurrent decay was 40 seconds would minimize any errors due to carrier recombination during the course of the measurement.

By comparing the peak photocurrents produced by flash illumination in heavily doped and in undoped phthalocyanine samples, it was found that an approximately ten fold greater peak current was obtained with the doped material than with the undoped material. Therefore, if the charge-carrier mobilities in the two systems were the same, this would require[24] that the quantum yield for charge-carrier production in the undoped material be about 10% of that for the doped material (that is, approximately 0.1). However, because of the concentration dependence of mobility,[15] one would expect that carrier mobility in doped phthalocyanine would be smaller than in undoped material, as a result of the higher dark-carrier concentration in the doped samples. Thus, the intrinsic quantum yield for undoped phthalocyanine is probably lower than 0.1.

It was noted that doping produces a 10^5-fold increase in steady-state photocurrents, but only a ten fold increase in flash-induced photoconductivity is observed. This may be attributed to the fact that the use of a short-duration light pulse to produce charge carriers tends to eliminate effects caused by differences in recombination times in the two systems, whereas steady-state experiments accentuate these differences.

The considerations presented in this section indicate that the over-all result of adding a strong electron acceptor to a phthalocyanine film is to increase the quantum yield for charge-carrier production and to increase charge-carrier lifetime. Thus, the ortho-chloranil negative ions act as efficient centers for the conversion of electromagnetic energy (which may be absorbed by phthalocyanine molecules situated many molecular diameters away) into charge carriers, and also act as effective electron traps. Similar, but apparently less effective, impurity centers existing in small amounts in undoped phthalocyanine could be responsible for its photoconductivity. Alternatively, the host molecules themselves could function as ionization centers.[25]

The present results indicate that the presence of electron-accepting impurities in organic semiconducting systems will increase the probability of utilization of charge carriers for chemical or biological processes by making recombination less probable and by increasing quantum yields. These factors would tend to counteract the effect of low carrier mobilities. This may have significance for photosynthesis in plant materials, in which the efficiency of utilization of electromagnetic energy for chemical processes is high.

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[24] The rise time of the flash photocurrent (about 3 µsec) is considerably smaller than the decay time (Fig. 7) and therefore errors due to carrier recombination are minimized by using the peak photocurrent in the comparison. Thus the ratio of the peak flash photocurrents should approximate the ratio of the quantum yields.

[25] L. E. Lyons, J. Chem. Soc. 5001-5007 (1957).