FEB 11 1965
SEP 11 1965

000-2085

FEB 8 1965

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MOLECULAR COMPLEXES OF FLAVINS AND PHENOLS. II.
ELECTRICAL AND MAGNETIC PROPERTIES OF CRYSTALLINE SOLIDS

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REPORT
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RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

Introduction

In recent years, studies of the electrical and magnetic properties of solid donor-acceptor complexes, mainly of the charge-transfer type, have received considerable attention. Interest in this type of investigation has been stimulated by, among other things, the recognition, initially made by Szent-Gyorgyi (1), that interactions of the donor-acceptor type may be quite common in biological systems. Thus, an understanding of the charge transport properties of the model systems, and particularly of the correlation of these properties with the behavior of the unpaired spins which are often detected in these systems by means of electron paramagnetic resonance (EPR), might provide insight into some of the energy transfer and storage mechanisms of living organisms.

* This work was supported in part by the United States Air Force Cambridge Research Laboratories (Contract No. AF 19(628)414) and by the United States Atomic Energy Commission (Contract No. AT(11-1)908).

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FEB 11 1965

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Studies of hydrocarbon-halogen complexes (2), amine-quinone complexes (3), and of several other systems, have indicated that these materials in the solid state have electrical conductivities which are higher than those of the components by six to twelve orders of magnitude. Furthermore, many of these solid complexes possess unpaired spins in concentrations much higher than those in the component solids, if they exist at all in the latter. So far, very little correlation has been obtained between electrical conductivity and paramagnetic behavior, except in the case of the pyrene-iodine and perylene-iodine systems (2c, 4) in which the unpaired spins have been identified as the charge carriers.

The most varying types of results have been obtained regarding the temperature-dependence of the EPR absorption in these complexes. Theoretically, in the absence of any spin correlation, a doublet state, and hence a Curie $1/T$ dependence, is expected. If there is any coupling between the spins, splitting into singlet and triplet states would result, and thermal production of unpaired spins as a consequence of singlet-triplet excitation (providing the singlet is lower in energy than the triplet) would take place. Singer and Kommandeur (4) have observed such an exponential temperature dependence of the spin concentration in hydrocarbon-iodine complexes, the thermal activation energy for the spin content being the same as that for the electrical conductivity. In the same systems at low temperatures, a small temperature-independent population of trapped spins (or free radicals) was noted. Similarly, Ottenberg et al. (5) observed an exponential temperature behavior for the spin content of the *p*-phenylenediamine-chloranil complex. However, in this case the activation energy was one-third that observed for the semiconductivity. Strictly temperature-independent spin concentrations have been observed by

Bijl et al. (3a) in several amine-quinone complexes. Chestnut and Phillips (6) obtained, for the diaminodurene-chloranil complex, an activation energy for conductivity of 0.25 ev and a spin concentration activation energy of 0.15 ev. Huggins and LeBlanc (7) have found for the β -carotene-triiodide complex a weak and essentially temperature-independent EPR signal intensity. Similar results were observed by Eastman et al. (8) in perylene-chloranil.

There is some inconsistency in the literature regarding the existence of hyperfine structure in the EPR spectra of charge transfer solids. Bose and Labes (9) reported such structure in a number of powdered amine-quinone complexes. Ottenberg et al. (5), however, could not find any evidence for hyperfine interaction in the EPR spectra of *p*-phenylenediamine-chloranil. Furthermore, they also observed that the spin concentration was independent of the method of preparation. On the other hand, Matsunaga and McDowell (10) have reported that the shape of the EPR absorption in some amine-quinone complexes was dependent upon the way in which the sample was made.

In view of these conflicting reports, it is evident that more work is needed before the behavior of the unpaired spins in charge transfer solids is understood.

The present work involves the study of the dark and the photo-conductivities and of the EPR behavior of solid flavin-phenol complexes. The charge transfer nature of these materials has been discussed in Part I (11). The most detailed work was done with the riboflavin-hydroquinone complex.

To the best of our knowledge, this work represents the first study of the photoconductivity behavior of single crystals of a charge transfer complex. The only other work on photoconductivity in charge transfer complexes was reported recently by Akamatu and Kuroda (12). These workers investigated

the spectral response and the temperature dependence of the photoconduction (activation energies were in the range 0.17 - 0.25 eV) in microcrystalline powders of complexes of pyrene with tetracyanoethylene, bromanil and 1,3,5-trinitrobenzene. Furthermore, the present study represents the first detailed investigation of the electric and magnetic properties of complexes in which both components are biologically-significant materials.

Experimental

The preparation and growth of large crystals of the complexes have been discussed in Part I. For all of the conductivity measurements, what appeared to be single crystals were used. However, no crystallographic examinations were made to assess the degree of perfection of the crystals.

The circuit diagram for the conductivity measurements is shown in Fig. 1. The voltage from a battery is applied across the sample and the resulting current flow is either measured directly in a Keithley microvoltammeter (Model 150A) or sent through a known resistance and the voltage drop measured in a Kintel microvoltmeter (Model 202B).

In the conductivity cell, the crystal was glued, by means of plastic cement, to the top of a glass rod which was mounted rigidly on a plastic base. The two electrodes were fixed to movable plastic blocks and could be made to approach the crystal from opposite directions. Ball-headed platinum wires were used as the electrodes. Aquadag, copper paint or silver paint were used to establish contact between the crystal and the platinum wires. With each of these materials, an initial large drop in the dark conductivity was noted after contact was made (see below for discussion of this).

Inasmuch as the complexes contained HCl, aquadag was chosen for use most of the time, rather than the metallic paints, although essentially no

differences in behavior were noted when the latter were used. However, aquadag itself tended to produce some decomposition on the surface of the crystal. This could be overcome by acidification of the aquadag with concentrated HCl before use.

In some experiments, grounded guard ring electrodes, prepared by placing copper paint completely around the central portion of the crystal, were used.

The conductivity cell was enclosed within an insulated glass chamber which in turn was kept inside a metal container. The temperature of the cell chamber was controlled by blowing hot or cold dry nitrogen gas through it. A thermocouple, placed close to the crystal, was used to record the temperature.

For measurements of photoconductivity, a 500 watt tungsten filament projection lamp was used as a source of light. The lamp output was filtered through a 4 cm. thick water filter, converged by means of a set of glass lenses, again filtered through a set of four infrared filters, and finally allowed to fall on the sample through a window in the conductivity cell holder. The photocurrent generated in the sample was allowed to flow through a known resistance and the voltage drop across the latter was amplified first in a Kintel microvoltmeter and then in a Sanborn DC preamplifier (Model 150-1800). The output of the preamplifier was recorded on a Sanborn recorder (Model 151-100A). This arrangement permitted the accurate measurement of rise and decay curves for photoconductivity. In general, it was found that the time required to reach a steady state after the light was turned on was of the order of seconds.

The white light intensity dependence of the photocurrent was measured by placing Corning neutral density filters in the optical path.

The effect of various wavelengths of light on the photoconductivity was measured using a Bausch and Lomb monochromator (Model 33-86-40-01). The

relative intensities at various wavelengths were calibrated with a thermobile (Kipp PI).

A Varian Model V-4501 EPR spectrometer, equipped with 100 kilocycle modulation and a temperature control unit, was used for the EPR measurements. Unpaired spin concentrations were estimated using solid diphenylpicrylhydrazyl as a standard. Spin content was assumed proportional to signal height times signal width squared.

Results and Discussions

The results of elemental analyses of well-dried samples of the solid complexes (see Table I) indicated the presence of one mole each of flavin, phenol, and HCl. These analyses vary somewhat from batch to batch, principally because the last traces of solvent are extremely difficult to remove. Consistent with this, the HCl content of undried samples (or incompletely dried samples) is always somewhat higher than that of dried preparations.

The 1:1:1 stoichiometry of the solid complexes is in agreement with what is observed in solution (see Part I).

When dissolved in water or ethanol, the solid complexes dissociate into the components. An examination of the visible and UV spectra of solutions in distilled water of the solid riboflavin-hydroquinone complex revealed the presence of uncomplexed riboflavin and hydroquinone and the absence of detectable amounts of any other organic materials (e.g., benzoquinone).

The concentrations of the riboflavin and hydroquinone in several solutions of this type, prepared from different batches of complex, were determined from the absorbance data at 445 m μ and 295 m μ and the results confirmed that the molar ratio of these two components in the complex was 1:1

TABLE I

Elemental Analysis of Flavin-Ethanol Complexes

a - Riboflavin-hydroquinone dried for several hours at 60°C under high vacuum

	Calculated for $C_{23}H_{27}O_8N_4Cl$ (1:1:1) (%)	Found (%)
C	52.82	52.38
H	5.20	5.45
N	16.71	16.61
O	24.48	26.04 (by difference)
Cl	6.78	5.52

b - 9-methyl isoalloxazine-1,4-naphthalenediol dried for several hours
at room temperature with P_2O_5 under high vacuum

	Calculated for $C_{21}H_{17}O_4N_4Cl$ (1:1:1) (%)	Found (%)
C	59.4	57.81
H	4.0	4.14
N	15.1	15.26
O	13.2	12.84
Cl	8.3	9.32

The establishment of good, stable, reproducible electrical contacts between the electrodes and the crystal proved to be difficult. After a contact was made, the observed dark currents generally showed large decreases with time, sometimes by two or three orders of magnitude, irrespective of whether aquadag or the metallic paints were used. That this drop was not due to either electrolysis or to polarization effects was shown by two observations. First, upon reversing the polarity at any stage of the decrease the magnitude of the dark current remained unchanged. Second, approximately the initial signal level could be obtained by remaking the contacts with fresh electrode materials.

When dry gases such as nitrogen or oxygen were passed over the crystal, the rate of decrease in the dark conductivity was enhanced. On the other hand, when moist air was used, the dark signal increased, and in some cases, when the moist air was introduced after a drop had already occurred, the dark current increased by a factor of ten or more.

All of the above observations can be accounted for simply by assuming that the initial decrease in the dark conductivity with time was due to a drying out of the electrode materials with an accompanying loss of contact.

To test whether surface conductivity effects were important, a grounded copper guard ring electrode was placed around the middle portion of the crystal. Only very small differences in current were observed, indicating little or no surface effects.

Due to the above-mentioned contact problems, it was not possible to obtain accurate values for the absolute magnitude of the conductivity. Thus, we have taken the highest observed value as a lower limit to this quantity. Table II gives some results for the room temperature specific resistivities of several complexes obtained in this way.

TABLE II

Specific Resistivities of Some Flavin-Phenol Complexes

<u>Complex</u>	Room Temperature Specific Resistivity (ohm cm)
riboflavin (pressed pellet)	$> 5 \times 10^{12}$
riboflavin-hydroquinone (single crystal)	1×10^5
riboflavin-resorcinol (single crystal)	2×10^8
lumiflavin-hydroquinone (single crystal)	2×10^{10}
9-methyl isoalloxazine-hydroquinone (single crystal)	7×10^7

The temperature dependence of the dark conductivity was measured after a steady-state had been obtained and there was no further decrease in the conductivity with time. A typical plot of the specific conductivity vs. the reciprocal of the absolute temperature for the riboflavin-hydroquinone complex is shown in Fig. 2. The activation energy* for the dark conduction is 1.1 ev. This was reproducible within ten percent. This value is somewhat high compared with activation energies which have been obtained in other systems (e.g. 0.019 ev in perylene-iodine and 0.15-0.65 ev in the amine-quinone complexes).

It was found that Ohm's law was obeyed by both the dark and the photo-currents in the range 200 volt/cm to 800 volt/cm (see Fig. 3). At larger field strengths, the current was proportional to some higher power of the voltage.

One of the most interesting and unique features of the photoconductivity of the riboflavin-hydroquinone complex is that its steady-state magnitude remains proportional to the magnitude of the dark current under a variety of conditions, e.g., at different field strengths and also at different temperatures. Thus, the activation energies for the magnitude of the dark and of the steady-state photo-conductivities are the same (see Fig. 2). If we assume that this identity of the activation energies is a result of the same process being affected by temperature in the dark as in the light, this would

*The equation used for the calculation of the activation energy was $\sigma = \sigma_0 \exp(-E/kT)$, instead of $\sigma = \sigma_0 \exp(-E/2kT)$. The use of the latter equation would imply that organic semiconductors are basically similar to the intrinsic inorganic semiconductors. However, statistical arguments presented recently by Fox (13) indicate that, because of the molecular nature of the excitation process in the organic materials, as opposed to excitations between bands in the inorganic substances, the factor of one-half would be inappropriate in the conductivity equation for organic semiconductors.

suggest that the thermally-activated process is not charge carrier production but rather is associated with phenomena involving preformed carriers in the crystal. A reasonable physical interpretation of this would involve the trapping of charge carriers immediately after their formation in the light and thus the rapid establishment of a steady-state with respect to carriers in the traps and in the conduction band. The magnitude of the photocurrent at any given temperature would be determined by the number of carriers in the conduction band. The thermal activation would then be associated with the detrapping process and the activation energies would be a measure of the depth of these traps.

Fig. 4 gives the kind of curves obtained on the recorder for the photocurrent rise and decay and Fig. 5 represents typical similar plots obtained from these. It is apparent that first order kinetics are obeyed. This demonstrates that recombination processes are not rate-limiting. Such a conclusion is further confirmed by the linear light intensity dependence of the photocurrent (see Fig. 6).

The unimolecular rate constants for rise and decay are independent of the light intensity (and thus of the rate of formation of carriers) and are also virtually independent of temperature, any activation energies being less than 0.1 ev. Thus, the rate of rise and decay of the photocurrent and the magnitude of the current in the steady-state are determined by different processes.

Interpretations of the temperature-dependence of the photoconductivity of organic crystals in terms of trapping phenomena are quite common (14, 15, 16). However, the activation energy found in the present system is as much as an order of magnitude larger than is normally found.

In Table III are given some values, obtained under various experimental conditions, of the photocurrent rise and decay constants. These are reproducible within ten percent under the same conditions. The rate constants were found to be functions of the distance between the two electrodes. In general, the closer the electrodes, the larger the rate constants. This would suggest that the magnitude of the constants is determined by the product of the average intrinsic velocity of the charge carriers and the reciprocal of the number of scattering centers* that the carriers meet in the course of their motion across the crystal; that is to say, the rise and decay of the photocurrent would be determined by the rate at which carriers can migrate through the crystal. The greater the distance they traverse, the greater is the number of scattering centers they meet, and hence the rate constants are smaller. Further evidence in favor of this point of view is provided by the following observations. The rate constants are found to be larger if the region of the crystal in the immediate vicinity of two electrodes is uniformly illuminated than when only one electrode is exposed to light. In the latter situation, the carriers would have to migrate through a longer path to reach the electrode. Furthermore, in crystals which had been vacuum-dried at 60°C, both the rate constants were found to be smaller than in undried crystals. This could simply be explained in terms of the production of scattering centers at the imperfection sites produced by the loss of solvent.

The kinetic picture which emerges from these results, then, is as follows. After the light is turned on, the rate at which a steady-state is established with respect to the population of carriers in traps and in the

*By scattering center is meant any structural feature of the crystal which influences carrier migration.

...the rate of rise and decay of the photocurrent will be determined by the rate of rise and decay of the photoconductive current. Thus, the rate of rise and decay of the photocurrent will, at any given temperature, be determined by the trap depth. However, the rate of rise and decay of the photocurrent will be determined by factors which effect the migration of carriers throughout the crystal and hence the time required for carriers to reach the electrodes and become discharged.

The mobility of the charge carriers, as measured by the photocurrent rate constants, was found to be essentially independent of the orientation of the crystal in the electric field. Also, the fact that no activation energies were found for the photocurrent rate constants suggests that the carrier mobilities are temperature-independent in the range 25° to 50°C. This is consistent with the work of Kepler (17) who has observed only a very small temperature effect on charge carrier mobilities in anthracene crystals.

To determine the sign of the majority charge carrier, one of the electrodes was illuminated and the photocurrent observed. On reversing the polarity of the illuminated electrode, both the kinetics and the magnitude of the steady-state photocurrent remained unaffected. This would indicate that both electrons and holes are equally responsible for charge conduction in this complex. This is in contrast to the perylene-iodine complex in which electrons are the majority carriers (3d) and to the naphthoquinone complexes in which holes carry the majority of the current (3c, 3d, 5).

The above picture of a photocurrent composed essentially equally of positive and negative carriers with a rate-limitation imposed by carrier migration is consistent with the observed first order kinetics of rise and decay

The information gathered thus far is insufficient to unequivocally identify the sites which act as the traps for the charge carriers. However, it would seem likely that the chloride ions could function as traps for the holes and that the protonated riboflavin could perform a similar function for the electrons. Furthermore, the kinetic results discussed above suggest that sites of imperfection in the crystal lattice can also function as carrier traps.

The action spectrum for the steady-state photocurrent was found to extend over the same range of visible wavelengths as the absorption spectrum of the crystal (see Part I). However, the former was considerably broader and flatter than the latter. This is to be expected in view of the fact that the complex crystal is almost black, so that light of all wavelengths in the absorption region of the crystal would be essentially completely absorbed. Thus, it is not possible to unequivocally establish which of the excited states of the complex can contribute to charge carrier production.

Crystals of the complexes were generally found to be paramagnetic. EPR spectra of single crystals of the riboflavin-hydroquinone complex showed hyperfine structure, whereas the powdered samples gave a single line spectrum which was about 20 gauss wide from peak to peak (see Fig. 7b). Bose and Labes (9) have also observed hyperfine splittings in the EPR spectra of crystalline powders of some amine-quinone complexes. In addition, they reported the presence of a definite hyperfine axis in a diaminodurene-chloranil single crystal. We have also observed a definite anisotropy in the case of riboflavin-hydroquinone single crystals. Thus, the shape of the EPR spectrum changed as the orientation of the crystal with respect to the magnetic field was changed. The most well-resolved spectra were obtained when the magnetic

the spin concentration was found to be independent of the amount of solvent in the sample. It is not possible to interpret the spectrum in terms of the distribution of the unpaired electron in the crystal.

We have also studied the temperature dependence of the EPR absorption of powdered samples of the riboflavin-hydroquinone complex. Below room temperature, samples which had not been vacuum-dried at higher temperatures approximately followed the Curie $1/T$ law. But when such a sample was heated to above room temperature, the spin concentration began to increase almost irreversibly, the rate of increase becoming very large in the temperature range 60-70°C. Samples could not be heated beyond 80°C because of decomposition. If a sample was kept at 70°C for a prolonged period, the spin concentrations increased by factors which varied from 5 to 20, depending upon the batch from which the sample was taken. During this heating period, some solvent was found to be given off. This solvent was so tightly bound to the crystal that it could not be removed by pumping at room temperature for six hours under a high vacuum (10^{-6} mm of Hg). However, if the sample was heated during the evacuation period (e.g., a 3-4 hour pumping at 60°C) most of the solvent could be removed. No further solvent was given off when this dried crystal was heated for a prolonged period at 70°C at ordinary pressures. In addition, there was no further increase in the spin concentration. The magnitude of the increase in spin concentrations resulting from either heating alone or from vacuum drying at higher temperatures was the same within the same batch of the sample.

If a dried sample was incubated with aqueous HCl for several hours, the spin concentration was found to decrease to some extent. The decrease was even more pronounced when an undried sample, after being heated for several hours

in contrast to the liberated solvent for the former. The effect of solvent removal was partially reversible.

A vacuum-dried sample showed a $1/T$ dependence of the EPR signal in the temperature range 80°C to -130°C . Below -130°C , the curve started to level off (see Fig. 5). It is possible that at very low temperatures, a temperature-independent EPR absorption exists, similar to that observed by Mastman *et al.* in the perylene-chloranil complex (8). The significance of this is unclear.

The EPR absorption in the riboflavin-hydroquinone complex was found to be structure-sensitive, as has been observed by Akamatsu and Kuroda (12) for pyrene-tetracyanoethylene and other complexes. The most slowly-grown crystalline samples were found to show the lowest EPR absorption. Furthermore, the increases in spin concentrations upon heating or upon evacuating at higher temperatures were largest in these samples. These observations, coupled with the above results, suggest that the paramagnetism is associated with lattice imperfection sites at which a complete transfer of an electron from donor to acceptor occurs.

The maximum spin concentration observed in a well-dried sample corresponded to approximately one mole percent of the complex. This is comparable to the values obtained in other charge transfer systems.

As we have seen above, vacuum drying also affects the photoconductivity of the hydroquinone complex. Thus, it is possible that the same imperfections which give rise to complete electron transfer also can act as charge carrier scattering centers.

Illumination was found to have no effect on the EPR absorption. Thus, charge carrier production could not be detected by the EPR technique.

may be due to a low charge carrier concentration compared with the trapped carrier concentration. This has been observed in many other charge transfer solids (3d). Similarly, effects of dry nitrogen or oxygen or of moisture on the EPR absorption were non-existent.

Grinding of a large crystal into powder did not affect the spin concentration, as was also observed by Eastman et al. (8) in perylene-quinone solids. This indicates that grinding does not produce the kind of imperfections which allow electron transfer processes to occur.

Conclusion

The results reported here tell us very little about the mechanism of charge carrier production, either in the dark or in the light. One could speculate that a small fraction of the complexes have, in the dark, because of interactions peculiar to the solid state, undergone a complete electron transfer process from phenol to flavin. The resulting electrons and holes could migrate through the crystal lattice and become trapped at imperfection sites or at centers of electrical charge (ions). Thermal release of the trapped carriers into the conduction bands would account for dark conductivity. Illumination, by inducing donor to acceptor transfer, would increase the conductivity by a similar mechanism. The EPR absorption in the solid complex could be a result of electron transfer processes which, because of the nature of the lattice sites at which they occur, lead to non-delocalizable unpaired electrons. These species would not be able to contribute to the electrical conductivity, but they could possibly function as trapping or scattering centers for charge carriers.

It is not immediately apparent what the relationships are, if any, between the processes reported here and biological energy conversion. However,

Photocurrent - arbitrary units

5.4

Photocurrent - arbitrary units
log scale

Steady state photocurrent - arbitrary units

11.5 gauss

Fig. 7a

11.5 gauss

Fig. 7b

E.p.r absorption intensity - arbitrary units

Fig. 8