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PUERTO RICO NUCLEAR CENTER

SOLID STATE PHYSICS PROGRAM

RADIATION DAMAGE IN ORGANIC CRYSTALS

Progress Summary Report No. 1

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STUDY OF RADIATION DAMAGE IM ORGANIC CRYSTALS USING ELECTRICAL
?CONDUCTIVITY

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Introduction:

This project is concerned with the effects of radiation on organic crystals. It is felt that such studies on well defined crystalline structures can provide firm foundation for a later study of more complex materials including those of direct biological interest.

The initial phase of this work consists in the study of the effect of neutron irradiation on the electrical conductivity of anthracene crystals. The choice of electrical conductivity is based on evidence that

this parameter is most sensitive to the presence of impurities or

fects

It should, therefore, become possible to detect quantitatively radiation damage at levels far lower than those that can be observed by

other chemical or physical techniques

At some upper level of radiation

damage it should be possible to correlate the electrical properties

directly with optical and other properties of the crystals, thus providing

an enlarged spectrum for the evaluation of radiation damage

The choice of anthracene as initial material for study is

predicated upon the fact that this substance has been studied more than any other organic material and its preparation in single crystal form is

relatively simple (2).

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The effect of neutron irradiation on anthracene has been studied previously by Komandeur (3,4), but to our best knowledge, no other work on this subject has appeared since then. Since Komendeur's work was done very early in the history of organic conductivity, we felt that it would be valuable to reopen and expand this work to include more recent developments such as the introduction of charge-injecting electrodes (5), and the application of space-charge-limited current theory to organic crystals (6,7). Below is a summary of the results obtained during the first six months of operation (January-June 1963) of this project

SECTION 1. RESULTS OF PRELIMINARY WORK AND DISCUSSION

Using the Kallmann-Pope technique (2), we have grown single crystals of anthracene using Eastman-Kodak anthracene X-480 and H-460.

They range in thickness from 10 to 70 μ and from 0.3 to over 1 cm in area

These crystals were obtained from ethylene chloride and xylene as received

from the supplier (Gastman) and also after redistillation in an all glass

apparatus, No significant differences have been found between crystals

grova using the solvents as received and after they were redistilled.

Xalimann-Pope cells (8), are now available commercially® and

three of these cells have been purchased. We have found these cells very

convenient to use because of the ease with which the electrolyte electrodes

can be removed and reestablished without introducing any noticeable change

in the system, Using these cells, an Osram HB0 100 watt lamp, several

soordair Co., 2 Clover Lane, R.D. 2, Dover, New Jersey.

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Corning filters and a Cary 31 vibrating reed electrometer, « few of the

Results reported in the Literature have been confirmed. This part of our work has enabled us to test our equipment and to familiarize ourselves with

the subelements

of the techniques.

Dark conductivity measurements, using 1M NaCl in both sections of the Kalimann-Pope cell, have shown that the electrodes are completely

symmetrical, that 41

the current flowing when one given side was at a

Positive potential (i_+) was equal to the current flowing when that same

side was at a negative potential (i_-). These results are shown in Table T.

TABLE 1.

SYMMETRY OF CONTACTS (Dark Current)

Applied:

Voltage : :

(volts) 2×10^{13} amp $> \times 10^{13}$ amp:

2 8.0 P80 :

10 3210 32.0

30°: 60:0 2 160.0

100 300-0 30:0

130: 400.0 2 400:0 :

Ho: 400.0: 00:0

We also found that the current-voltage relation (in the dark) was ohmic up

to 100,000 volts/cm and that the resistivity of anthracene is of the order of

10^{14} ohm-cm. The results are identical to those obtained by Pope and Kalleann

(9). (See Fig. 1).

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As was found by all other investigators (9,10), we observed that

the photocurrent flowing when the illuminated face of the crystal was at

positive potential (+) was larger than when the illuminated side was

negative (1-). To observe these photocurrents we used IM NaCl in both cell compartments and the Light source of 3650 A. The results are plotted

in Fig. 2 and the observed asymmetry is generally considered to be a consequence of the predominance of positive charge carriers, i.e. holes

in anthracene. This is another confirmation of Pope and Kallmann's results (9).

Measurements with other electrode systems, such as IM NaT saturated

were made and the ratio I_{+}/I_{-} was found to change drastically,

as may be noted when comparing Tables IT and IIT,

TABLE IZ.

HOLE INJECTION THROUGH ANTHRACENE

Applied 3650A Photocurrent

Voltage (no fodine)

(volts) : :

s+ 1010 emp tt? x 10! amp: at/in

2 100 29 3.6

wo: (2050 810 2 256

20 3200 110 2291

50 3300 19.0 1%

+200 3500 50.0 275.0

it and 17 refer to currents measured when the polarity of the side thru which the 3650A Light entered was positive and negative respectively.

Intensity of 3650A light: 170 pps

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TABLE TIT

HOLE INJECTION INTO ANTHRACENE

Applied 43608 Photocurrent

roleage (odine electrode) :

s(voles) : : : :

st x10! amp tr x 1010 amp sate

2: 0.33 : 0.07 ane

wah : 0.10 240

2 = 105 18 583

50: 500 oat : 12200:

2200: 2700. 2 2.0. 21350

i_+ and i_- refer to currents measured when the polarity of the face of the crystal in contact with the iodine was made positive and negative, respectively.

Intensity of 360A Light: 450 44 watt/ ca?

Kallman and Pope (5) were the first investigators to observe the role played by iodine and to propose a mechanism by which iodine extracts an electron from anthracene, thus injecting a positive hole into the crystal. These results were discussed quantitatively by Kallmann and Pope (11) and also by Mark and Helfrich (6). The latter investigators believe that the free holes injected into the anthracene crystal can act as a virtual anode when the injecting contact is biased positive and the space-charge-limited hole currents follow. If this is so, then the currents observed by us using the iodine electrode are space-charge-limited, Fig. 3 shows the steady-state current-voltage characteristic of anthracene observed in our laboratory. It differs slightly from the one published by Mark and Helfrich (6) who used anthracene doped with tracer of tetracene and a band of 3600-4000 Å.

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(On the other hand thi

same investigators report curves similar to ours

4m cases of pure hydrocarbons where the band employed to excite the electrode

does not produce photocurrents in the crystals, The slight curvature observed by Mark and Helfrich and its absence in our work is attributed to the fact that our measurements were performed with 4360 Å light to which anthracene

4a is practically transparent (10) and therefore free holes were being

injected at the anode only, while Mark and Helfrich were generating free holes nonuniformly throughout the bulk of the crystal due to the light they used.

Fig. 3 shows that crystals grown from anthracene grades H-480 and X-480 gave similar results.

Before starting the study of radiation damage we checked the reproducibility of our experimental technique by removing the electrolyte electrodes after each measurement and replacing them just before the

following measurement. The results shown in Fig. 4 demonstrate the reproducibility over a period of several days.

The effect of crystal thickness was also studied (Fig. 5)

and the displacement in the curves of the different crystals follows the

current-volts

response predicted by the theory of space-charge-limited

currents as applied to organic crystals (6). The fact that crystals of

different thicknesses give about the same saturation current seems to

indicate that surface generation is the dominant mechanism of carrier

formation.

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SECTION IT. RADIATION DAMAGE MEASUREMENTS

In the initial stage of this investigation we are limiting the

Irradiation studies to the effects produced by neutrons from a 1 curie Pu-Be

source delivering 1.5×10^5 n/sec, Using this neutron source, the anthracene
crystals were irradiated with (a) fast neutrons only, and (b) with a mixture
of fast and thermal neutrons. Returning to the results shown in Fig. 5 it

can be seen that before irradiation different crystals produce the same slope

of the straight line portion of the curve and that the value of the saturation

current is also more or less the same. In accord with Mark and Helfrich's

(6) theory, the value of this slope indicates a space-charge-limited current
influenced by trapping. Furthermore, there is a relationship between the
energy distribution of the traps and the slope of the curve, and between

the concentration of the traps and the magnitude of the current.

Fig. 6 shows the behavior of the crystals after irradiation, and it is noted that the steep portion of the current remains unchanged but that the saturation level is very much increased. The increase was so large that

the saturation current exceeded that capable of being measured by our instrument. This behavior was observed with crystals irradiated by placing them on top of the neutron source removed from the paraffin box which is normally used for radiation protection.

Crystals were also irradiated by placing them on top of the neutron source while it was

inside the paraffin box. Under these

conditions the saturation current was also enhanced (Figs. 7A and 7B),

but notably to a considerably smaller extent regardless of whether the

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ter

tion was carried out over a short or long period of time (compas

Figs. 7A and 7B). Here too, the slope as well as the magnitude of the current in the steep portion of the curve were unaffected by irradiation

Since the difference in the behavior of the crystals subjected to neutron radiation was thought to be due to a difference in the availability and action of fast and thermal neutrons under the two experimental conditions,

a shielding arrangement was devised by means of boral that exposed the

crystals only to fast neutrons. This was done by enclosing both the neutron

source and the crystals in a small boral box. Under these conditions the

effect of the radiation was identical with that obtained when the crystals

were exposed to the neutron source while the latter was outside the paraffin

box (compare Figs. 7A, 7B and 8)

Fig. 9 shows that crystals irradiated with fast neutrons also give a saturation current. This result was obtained by employing a wire mesh in order to reduce the intensity of the light source and consequently bring the current level down to the range of our instrument.

Besides the apparently different effects of fast and thermal neutrons another noteworthy observation is the ability of the irradiated anthracene crystals to recover the normal electrical behavior with time. This behavior is shown in Figs. 6-9 where the conductivity of a given crystal is recorded at different intervals of time after exposure to

neutrons.

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DISCUSSION OF RADIATION DAMAGE RESULTS

Unlike the previous work (3,4) on the effect of neutrons upon the conductivity of anthracene crystals, our experiments employ low doses of radiation. This approach is chosen in order to be able to observe the

gradual change in the radiation damage, and possibly differences in the

radiation damage mechanisms, as the crystals are exposed to increasing

doses of radiation, The results obtained so far indicate that doses of

the order of 10^7 n produce measurable effects

It is noteworthy that the only effect of neutron irradiation is

to change the level of the saturation current of the anthracene crystals

The fact that the slope and the magnitude of the steep portion of the current-voltage curve are not affected by the radiation indicates the absence of a volume effect, i.e. there is no change in the number and

the distribution of the traps. This behavior is not unexpected if one

considers the low doses of radiation which were employed and the fact that a change in concentration of 10^{10} traps/cm³ escapes detection (12).

?There remains the question of the change in the saturation current as a result of the radiation, and this is most probably a surface phenomenon.

Therefore we assume that the main effect of the neutrons is to produce protons by elastic scattering with the many hydrogen atoms of the hydrocarbon, then we can visualize the ejected proton coming to rest as a protonated anthracene molecule (TT-complex). At the same time the original collision should leave behind an anthracene anion. The resulting anion,

by virtue of its low ionization potential, is expected to react more

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readily with the iodine electrode than an ordinary anthracene molecule, and

in the process there are produced an iodide ion and the relatively stable

anthracene radical. The latter upon combining with the dislodged proton

produces an electron-deficient anthracene species which is identical with

the hole that is obtained in nonradiated anthracene crystals

It reacts with

iodine at the electrode contact. Thus, this mechanism suggests an explanation

for the increase in the currents that are observed with the crystals exposed

to fast neutrons

and accounts for the absence of changes in the number

and energy distribution of traps, since, once the hole is formed, the

transport mechanism throughout the bulk of the crystal is unchanged.

Furthermore, the mechanism explains the recovery of the normal electrical

behavior induced either by thermal neutrons or by rest at room temperature since either condition provides energy necessary to mobilize the dislodged Proton for return to the anthracene anion.

?Another possible mechanism for the enhancement of the saturation

current by fast neutrons invokes a dislocation of the surface molecules

?This amounts to an increase in the effective surface area and thus can account for the greater number of holes that can be formed at the contact,

The recovery mechanism in this

?simply involves the relocation of the

dislodged anthracene molecules to their equilibrium lattice positions with

the activation energy provided by thermal neutrons or environmental temperature,

ature,

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Finally, it can be suggested that anthracene anions, produced in accord with the first mentioned mechanism, favor the formation of an iodine complex more so than normal anthracene molecules. This is because

in the charge-transfer complex the anthracene species plays the role of an electron donor, and thus the presence of anthracene anions at the surface must enhance the hole injection process by favoring the diffusion of the

iodine to the surface.

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