

# PRNC038

PRNC 38

PUERTO RICO NUCLEAR CENTER

RADIATION DAMAGE IN ORGANIC CRYSTALS

Progress Summary Report No. 2

OPERATED BY UNIVERSITY OF PUERTO RICO UNDER CONTRACT  
NO. AT (40-1)-1893 FOR U. S. ATOMIC ENERGY COMMISSION.

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[STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS USING ELECTRICAL  
CONDUCTIVITY

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Progress Report #2

Work performed at Puerto Rico Nuclear Center

Rio Piedras, P.R., under U.S. Atomic Energy

Commission Contract T(40-i)-1833 (Project 14)

March 1964

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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 a firm foundation for a later study of more complex materials

including those of direct biological interest.

In the initial phase of this work we have studied 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 defects (1), our results

show that it is possible to detect quantitatively radiation damage at levels

far lower than those that can be observed by other chemical or physical

techniques. We expect that 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.

The effect of neutron irradiation on anthracene has been studied previously by Komandeur<sup>(3)</sup>, but to the best of our knowledge, no other work on this subject has appeared since then. Since Komandeur'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

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recent developments such as the introduction of charge-injecting

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electrodes ?, and the application of charge-limited current

(3,6),

theory to organic crystals

Below is a summary of the results obtained during the period

July 1963-December 1963.

## SECTION I. CRYSTALS

In order that our results could have @ meaningful statistical

interpretation it was nec

sty to produce our own crystals and for

this reason we established @ crystal growing station. In this station

we used the relatively simple technique described by Kalinann and Pope(7).

?This technique consists in preparing a saturated solution of anthracene in

1,2-dichloroethane at a temperature a few degrees above room temperature

?and then cooling the solution slowly to room temperature, The surface

Of the solution is covered with a few milliliters of xylene to prevent

rapid cooling at the surface. Xylene has a smaller density than dichloro-

ethane and if poured carefully it will float on top of the solution. Some

time during the cooling process crystals will be formed and if the proper

temperature gradient exists in the solution the crystals will neither

?sink to the bottom nor float to the surface. The crystals will grow

slowly and should be flushed out as soon

they attain an acceptable

size, TE the proper temperature gradient 1 not obtained the crystal

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aa

will sink before they grow to an acceptable size, At the bottom they

continue to grow but no longer as monocrystals and therefore cannot be used in our experiment. If the crystals produced are unacceptable, the solution cannot be reheated and cooled again to make second attempt

to get good crystals because the toluene mixes slowly with the dichloroethane making a less dense solution in which it will be more difficult

to get the crystals to float

our experience with the Kallmann-Pope technique to grow crystals

is that more often than not we fail to produce good crystals. Each

trial takes about half a day's work and many times our technician has

He has

spent weeks trying to grow crystals without any success

grom # total of 150 crystals ranging in thickness from 10 to 70  $\mu\text{m}$

and from 0.3 to over 1  $\mu\text{m}$  in area. Many of these crystals break in

the process of being mounted in the Kallmann-Pope cell or develop

4 leak while undergoing measurements

we have tried to grow crystals using @ modified Kallmann-

Pope technique using 1,2-dichloroethylene instead of 1,2-dichloro-

ethane, and cooling without covering the solution with xylene. The

1,2-dichloroethylene has a relatively high density and the anthracene



crystals float. After the crystals are fished out they are cleaned

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-6-

Some which sometimes adhere to

with xylene to eliminate smaller crystals:

the surface of the Yoreer crystals, Using this technique we have

from 25 crystals, Thus crystals are so large that sometimes they

can be broken into two or three pieces each one of which can be

used for a separate weighing

We have purchased from Hershey Chowicsi Co. unselected

anthracene crystals 10 mm x 10 mm x 0.3 mm which we have cleaved and

polished to thickness of approximately 0.3 mm, we have also purchased

from Warshaw Chemical Co. selected and polished anthracene crystals

10 mm x 10 mm x 0.3 mm and 10 mm x 10 mm x 0.3 mm. We have made measure-

ments on some of these crystals which are included in this report.

#### SECTION IV. RADIATION DAMAGE MEASUREMENTS

We have done electrical conductivity measurements on crystals

ranging in size from 10 to 100, which were grown in our crystal growing

station. We have also done electrical conductivity measurements on un-

selected Harshaw crystals which we cleaved and polished to a thickness

of approximately 200  $\mu$ s and on selected and polished Harshaw crystals of

300 p thickens, These measurements were done with the Kelimann-Popel®?  
cell using Wal-Nat, KCl-Mect, Na950, - (NeT-Tp) electrodes and 36508

and 43604 Light. The measurements were done before and after irradiating

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with our one curie Pu+Be neutron source.

the crystal

Fig. 1 shows measurements done on our crystal #54c) using the

Mal-I, electrode and Light of 4360A before and after irradiation with

neutrons. The curve showing  $\log I$  vs  $\log v$  after irradiation is not

complete because at that time our measuring instrument was a Cary 31

vibrating reed electrometer which was not capable of measuring the

high currents obtained. In addition to the Cary Electrometer we now

have a Keithley Electrometer Model 600A which allows us to read currents

we high as one ampere. Fig. 2 shows measurements done on our crystal #143

before and after irradiation in which the values of  $I_4$  after irradiation

were measured with the Keithley Electrometer. Figs. 3, 4, 5, show

measurements done on our crystals #5-6, #4-2(H), and #SH-1 using the

Nat-Tz electrode and a 4360A light source. Crystals #54 and #143

were grown using the Kallmann-Pope technique. Crystal #5-6 was grown

using our modified Kallmann-Pope technique. Crystal #A-2(H) was

cleaved and polished from a Horshew unselected crystal and crystal

Crystal #4 selected and polished Harchaw crystal of 0.3 mm thickness.

Fig. 6 shows measurements done on crystal #HC-1 using the

Na<sub>2</sub>SO<sub>4</sub> electrode and Light of 36504 before and after irradiation,

(a) The same measurements are shown in Fig. 6 of our Progress  
Summary Report No. 1.

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## SECTION III. DISCUSSION OF RADIATION DAMAGE RESULTS

The relevant experimental results are, firstly, that neutron

irradiation produces a significant increase in the conductivity of thin

crystals (10-50  $\mu$ ) when measured by means of the NaI-I<sub>2</sub> electrode and  
36504 Light source but not so when measured by means of the Na<sub>2</sub>SO<sub>4</sub>

electrodes and a 3650A Light source, secondly, that the elevated conductivity

8 gradually to normal preirradiation levels, and thirdly, that

neutron irradiation does not appear to induce exalted conductivity in thick crystals (0.3 mm) even when the measurements are carried out by means of the iodine electrode.

These results seem to indicate that the exalted conductivity depends on a surface phenomenon that involves an anthracene spectrum

activated iodine spectrum

activated by the neutron irradiation and

Produced by the 43604 light source. The difference between "thin" and

"thick" crystals can be explained in that 1/4 of the 43604 Light

reaches the face of the crystal exposed to the iodine solution in the

case rather

case of the "thick" crystal, since anthracene per

transparent to 4360 Å light, it is probable that scattering rather than absorption of light is responsible for such difference.

In the preceding report it was suggested that the effect of fast neutrons may well be due to dislocation of a proton from anthracene, and the formation of transient anthracene carbanions and anthracene-proton complexes. The following is a calculation of the increase in

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the photocurrent that may be expected to be produced under our conditions of neutron irradiation and measurements by means of the iodine electrode.\*

We estimate that after exposing a crystal to our neutron source for

approximately 70 hours the crystal receives a dose of the order of

$3 \times 10^{19}$  neutrons/cm<sup>2</sup>. Considering the cross section of hydrogen for neutrons of intermediate energy and considering the spatial distribution of the anthracene molecules in the anthracene crystal we estimate that approximately  $10^{14}$  dislocations per cm<sup>2</sup> were produced at the crystal surface after

18 70 hour period of irradiation. Now, we shall consider the magnitude of

the process intended to take place between the "excited" iodine

that the

molecules and the "excited" anthracene species. In a 1M solution of

Iodine there are  $6.03 \times 10^{23}$  molecules/Liter or  $6 \times 10^{23}$  iodine molecules per cm<sup>3</sup>. Rounding off the latter figure to  $10^{24}$ , we permit to estimate that there are  $10^{24}$  iodine molecules/cm<sup>3</sup> at the surface of the anthracene

crystal in contact with the 1M iodine solution. If the frequency of

used to

collisions between Iodine and the anthracene crystals faces is



be  $10^2/\text{sec}$ , then the number of collisions will be  $10^{15} \times 10^2/\text{sec}$  or

$10^6$  collision/sec cm<sup>2</sup>. A similar calculation following the procedure of

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Moelwyn-Hughes(9) gives the number of  $10^9$  collisions/sec cm<sup>2</sup> and the latter

value that,

figure will be employed in the calculations which follow. If we

the cross section of capture of iodine by an "excited" anthracene is

$10^{-15}$  cm<sup>2</sup>, then there is an area of  $10^4 \times 10^{-15}$  or  $10^{-11}$  cm<sup>2</sup> of "excited"

anthracene at the surface, and the number of successful collisions between

I would gratefully acknowledge the aid of Professor Martin Pope (Physics Dept  
New York University) in developing this numerical estimate.

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Iodine and "excited" anthracene are given by  $10^{29}$  e<sup>-</sup> (capture a

$10^{25}$  collisions/sec or  $10^{14}$  collisions/sec. Should each such

collision produce an additional carrier then the resulting current

would be  $10^{14} \times 1.6 \times 10^{29}$  electrons/sec =  $1.6 \times 10^{43}$  emps/e<sup>-</sup>.

In a crystal of 0.1 cm<sup>2</sup> surface this results in a current of  $1.6 \times 10^9$  amps.

This indeed is the magnitude of the "exalted" current which is indeed observed.

The effect of photoactivation on the iodine ~ "excited"?

anthracene interaction can be visualized in terms of an increase in

the probability of interaction by the "excited" iodine. We must first

calculate (see below) the distance from the crystal in the Iodine solution

which will permit an excited iodine to diffuse to the crystal surface

during the transit time of the carrier in the bulk of the crystal, The  
AT.

one of the equations is  $L = \sqrt{D \cdot t}$ , and letting  $t = 10^{-3}$  sec we

obtain  $L = 9.5 \times 10^{-5}$  cm and so  $210^\circ$  can be

the diffusion constant =  $L^2 / D \cdot t$ . the value of the Sump

region  $L = \sqrt{D \cdot t}$  where  $t$  is the jump time, From this equation and from the

value of the velocity of the iodine molecule one can calculate the value of

the jump length and the jump time, The jump length is estimated to be

a

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$10^{-7}$  sec and the jump time  $10^{-7}$  sec. we now estimate the transit time

of carrier in a  $10^{-4}$  cm thick gallium arsenide crystal when we apply 4 volts

across it

of so we have  $Q = 2$

for an iodine molecule with a jump time of  $10^{-10}$  sec

$= 3 \times 10^8$  Therefore in the

interval of  $10^{-8}$

Produces  $10^8$  jumps. If we place a given iodine molecule at  $10^{-4}$  cm from

the surface, it will probably hit the surface at least once during an

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?9

interval of time equal to the transit time, This then,  $10^8$  cm, is the  
distance in the solution which is taken for the calculation of the number  
of "excited" Iodine molecules which are produced by the absorption of  
light. With a molar extinction coefficient of  $10^4$  for 1 M iodine,  
 $6 \times 10^{23}$  molecules per mole  $\times 10^4 = 10^{27}$   
° and

$$V_{\text{ig}} = 1 = 0.9$$

Thus 10% of the light is absorbed, and with a light intensity of  $10^{14}$   
quanta/cm<sup>2</sup>/sec there will be  $10^{10}$  "excited" iodine molecules that can  
interact with the excited anthracene molecules at the surface of the  
crystal. We conclude, therefore, that there is ample reason why

4360Å Light increases the interaction between "excited" iodine and  
anthracene molecules and thus enhances the current.

It now remains to suggest the nature of the interaction between

the excited" species. As mentioned above, it is probable that neutrons

produce anthracene carbanions and anthracene-proton complexes, The

4360 Å Light is absorbed by iodine and most likely produces dissociation

of the latter into iodine atoms. These iodine atoms can be thought to

diffuse to the crystal surface (their diffusion rate will be even greater

than that of the iodine molecules) and there we can visualize the

of electron transfer which produces iodide

occurrence of the process

ions and

anthracene radicals,

SO ea

Teta:

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?This process represents  $\odot$  hole injection mechanism which is more favorable

than that which probably occurs in the dark,

Oe yee

Bea Bo

for which occurs when the anthracene has not been exposed to neutrons,

rate of Oe aay

2 (process in the dark)

ream ee Oe an

(process under illumination)

In the anthracene crystals containing dislocated protons, thermal

activation will eventually cause the return of the protons to the

anhrsey! carbentons: (84:4) 4 4: ae A+ Ast and ehke

explains the gradual Loss of the enhancement in the saturation current.

An alternate explanation of the effect of the 4360K light

source does not involve the formation of Iodine atoms but revolves

around the activation of a charge-transfer-complex at the crystal

surface, The anthracene-iodine complex absorbs light in that range(?)

and it can be assumed that a similar absorption will be given by the

charge-transfer-complex produced from an anthracene carbocation and iodine.

(6 an) ana (tye)

will be promoted by the absorption of light to the polar spectra

(to +4.9) on a (1

spectra then initiate a chain of electron transfer within the anthracene

Both kinds of charge-transfer-complexes

i) respectively, are the

crystal.



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one

#### ?SECTION IV. EQUIPMENT

In order to purify larger amounts of anthracene in connection with the growing of single crystals from the melt we have built @ vacuum system to repurify the anthracene we obtain from commercial sources.

used a Fisher Scientific zone refiner to further

Besides, we have purchased

equipment to purify the anthracene after purification by sublimation in our vacuum system, we have also built an oven to grow anthracene crystals from

the melt, Figs. 7 and 8 show our vacuum system, and zone refiner and

oven, respectively, which have been assembled in the laboratory.

We have also built the optical and electronic equipment,

necessary to do steady voltage-light pulse transient photoconductivity

and electronic equipment

measurements (Fig. 9) and other optic

pulse transient photoconductivity

ry to do steady light-voltey

urements. (Fip. 10).

ight pulse equipment

?The equiment for steady volta

alrency been tested and a ready to be used for transient photo~

conductivity measurements. The steady light-voltage pulse equipment, is being tested at present and should be ready for use in the near

future. Figs. 11, 12 and 13 show pictures taken with an oscilloscope

camera using our steady voltage-light pulse equipment.

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APPLIED VOLTAGE

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APPLIED VOLTAGE (voLTS)

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APPLIED VOLTAGE (voLTe)

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"APPLIED VOLTAGE (VOLTS)

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APPLIED VOLTAGE (voLTs)

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FIG. 10 EQUIPMENT TO DO STEADY LIGHT-VOLTAGE PULSE  
MENTS

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