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PUERTO RICO NUCLEAR CENTER

RADIATION DAMAGE IN ORGANIC CRYSTALS

Progress Summary Report No. 3

JH orenatao 8 UMvERsITY OF PUERTO RICO UNDER CONTRACT

NO, AT (401-1893 FOR U. 5. ATOMIC ENERGY COMMISSION

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STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS USING ELECTRICAL

conpuctrvity

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?vt Wetax?- Principal Investigators

Progress Report #3

Work performed at Puerto Rico Nuclear Center

Rio Piedras, P.7., under U.S. Atomic Fnergy

Comission Contract AT(40~i)-i833 (Project 14)

Senvary 1965

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?TABLE OF coNTeNTS

cryacale .

Currents .

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TamnooocrtoN:

?This project ie concerned vith the effects of radtatton on

organic crystala. It te felt chat auch studies on well defined cryatal-

Line

uctures can provide @ fire foundation for a later study of more

?couplex materials inciuding those of direct biological interest. We have

?chosen anthracene as the initial material for atudy because this subst

hhas deen studied more than any other organic material,

?The effect of neutron irradiation on anthracene has been studied

Previously by Kamandeur(!+?), nut eo the best of our knoviedge, no other

?work on this subject hae appeared since then. Since Komandeur's vork was

done very early in the history of organic conductivity, we felt that t¢

would be valuable to reopen and expand thle work to include more recent

developments such as the introduction of charge-injecting electrodes (),

and the application of spaco-charge-linited current theory to molecular

cexyntate(415+6,748,9,10,11,12)

Below 19 « sumary of the results obtained during the pertod

January 1964 to December 1964,

Our preliminary results of neutron radiation denage presented

4m our Progress Reports #1 and 42 indicated that in electrical conductivity

meaurenents a change in the

euration current ocoure after a very low

dose of radiation. These measurenents vere made using « Kalinann-Popa(!?)

cell with NayS0, solution as one of the electrodes and Nar-1, solution

% 2

the hole injecting electrode. Subsequent measurements with a wore sensiti

electrode system recently developed at our laboratory indicate thet the

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changes detected are most likely an electrode effect rather than &

change in the eryatal itself. However, our most recent work shove that after irradiating with gama rays or x-rays and making the

with the improved electrode aysten 4 definite change to the electrical conductivity of the crystals ta detected while no change was observed after neutron irradiation of doses comparable to those reported previously, These results comprise the main part

of this report.

SECTION 2. cavstans

?As Atscussed in Summary Report #2 we have used an improved Kattmann-Pope() technique to grov large anthracene crystals from solution. ?The min features of this techaique 18 to use a solvent

comprised of equal parts by volume of dichlorethane, c{s-dichloro-

?ethylene and trans-dichloroethylene and to carefully contro? the

rate of cooling of the solution. A complete description of this

technique vill be subsitted for publication in the near future.

Using chia technique ve have grom all the crystals needed

for our experiment, These crystals,

(approxisately 2 cn®), and appropriate thickness which ranges fron

20 to 100 microns, were especially suited for our measurenents.

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Ceyatals vere irradlaced ueing the following radiation soures

(a) Pu-te neutron source

(bo) the thermal coluan at the PRNC research reactor

(e) 4 Co-60 gamma ce

(3) © 120 kup x-rey radiotherapy unit

Our Pu-Re neutron source in 10 curte source imbedded in peratfin.

?Tee crystals ware placed right next to the source where the flux 16 epprent-

mately 2 x 105 n cn? sec! and the average neutron energy 1s approxinately

2Mev. Assuming the neutron absorption coeffictent of anthracene to be

spprorinately aqotl to that of aintlar orgente substances the neutron

radiation absorbed by anthracene ts epproxieately 3 x 109 rada/n/en?(!5)

where 1 rad equals 100 ergs/gm. Due to the fact that our Pu-Be neutron

source has such a emall flux the doses given in reasonably short tines

(3 days to 1 week) were of the order of # fev ra

?The crystals srradiated with the reactor were irradiated with

?thermal neutrons (.025 ev). The flux used was approximately 109 n/cn*/eec

?and the doses given ranged from 1000 to 12,000 rads approximately.

?The Co-60 gamma cell used co irr

ace our erystala hat

output

Of 780 r/min. and the energies of the Co-60 photons are 1.33 and 1.17 Mev.

By meeuring the absorption coefficient of anthracene for the Co-60 photons,

?which turned out to be 0.118 on?l, ve calculated chat the energy absorbed by

ithracene is 293 erge gal rl. The doses given ranged from 8 x 102 to 10° r,

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The x.

y untt used to treadiate our erystels w

2120 kwp

radlotherapy unit with an output of 325 r/min, By measuring the absorption

coctfictent of anthracene for this radiation, vhich turned out to be

1

0.671 en", ve calculated that the energy absorbed by anthracene ts

rl. the doses given ranged fron 8 x 102 x to 108 x,

296 erge gm

SECTION ITE. EXPERIMENTAL ser UP

?The experinent

set-up {6 shown tn Fig

?The electro

configuration systen chat ve have developed and used ia as follows,

?The non

injecting electrode consiate of a plece of transparent

conducting glass (evaporated tin oxide on one of the surfaces) on which 4 small drop of 1M NayS0, solution 16 placed. The crystal te then layed on top of the NapSC, solution drop which then spreads Producing @ very good electrical contact between the crystal and the conducting gisas. the injecting electrode on the opposite side of the

eryatal consists of a drop of Net-1, olution

eo whieh a platinum

wire te Anecr ted

veld im place by 9 simple snevtaced support. tn order that the ceproducibitty of the saturation value of the current be within a factor of two, the conceateatton of the Tp im the NAr-Tp solution has co be vithin well defined Limite. This concentration 4s

achieved by diluting «

eureted solution of Lo¢ine in IM Nal at room

temperature to 25-50% dilution, vith a saturated solution the

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-s-

Feproductbility of che saturation current values te very poor.

Voitages between 2 and 500 volts ware applied to the crystals

from a Keithley Model 240 regulated pover oupply. The current

measured using « Keithley Model 600A electrometer.

?The i1luatoation of the injecting electrode was achieved

using the ight from mercury lamp, (Osram #80 100 W/2) Tais Light

was pagsed chrough either a Corning Color filter #S 5-74,(),.= 63604")

oF through « Corning Cut-off flicer #CS 3-72 which euts-off at 4300A* or

through « $$ 3-70 which cuts-off at 490A". As te shown in Fig. 1 the path of the light, after leaving the filter, {# through the conducting

and crystal and then into the Nat-1, solution.

SECTION IV. EXPERDONTAL RESULTS

Typtoal current-voltage characteriatic curves on a log { ve

og V plot are shown in Pi

+2, The changing parameter in these curves

As the concentration of the todine in the NeI-Iy solution. The values

of each curve are the average values gotten from many successive measure-

ents on a crystal. Measurements taken on large number of similar

crystals give similar results. In all che measurements represented {2

Fig. 2 the electrod

Were not {lluminated, Fron measurements of thie

type 1¢ was found chat the iodine concentration most conventent for our measurenents is a 25% dtlution.

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Ko detectable changes vere shtatned after irradiectng the

eryatals with che soutren sources 12? Leatee 4m fa) and () of Section If

ing the doses iniictzed ia this scecion.

Fig. eseats the space clucee ieitad currence tna log

va Log V plot with une wishoue 42umtae. e Imjeccins electrode. The

Aodine coucencretion of ch: ?nfactine aleervude for al? our meastrenente

was 25% of che saturatet reise, Jo uhann a9 Pp. 2 rhe rapraduethliey

te good using this concentrac?on. ?urve i af Pig. 3 shove the results beained vhen the crystal was not (Jluninatec. Curve #1 shovs the

Fesulte obtained when the injecting electrode was i:lumtnated chrough

the Corning Color ftlter #3 5-74, vhich his « maximum exenamteaion at

D. = 4360". curves #1tr and SIV show the results obeatned when che

sngecting electrode was {Hluntnaced through che Corning Cut-off f1tere

fs 9-72, (out off ax = atoan'), and 4s 3-70 (cut off at A a4900%*y,

respectively. The relative dlsplacenents of these four curves ace

explained by the fact ehae the Light Lo parctally absorbed by the crystal

and part by the injecting odine electred

Av previously stated che injecting electrode was {1luminated

with light from a high peeseure lig source,* and

shown in Fig. 1 pa

frat through the color or cut-off fL1ter then through che crystal and

then is absorbed by the electrode. The displacement of curve IT of Fig. 3,

4m which the color filter was used, from curve I, taken in the dark, in the

* tmcenaiey with f8lter fe9 5-74 17Opuare/om?

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a

region below the saturation current, is explained by the fact chat part

of the light cransuicced by this filter 4s absorbed by the anthracene

crystal. This resulte in a redistribution betwees the free and crap;

carriers producing higher current values for the same voltages. The higher saturation values in the {itwminated cenes,(ts due co the

jorption of the li

in the iodine solution near the crystal surface

Anereasing the concentration of the disassociated todine.

In curve TIT, taking account of the absorption coefficient

of the anthracene and the transnission of the cut-off filter used,

lets Light te absorbed tn the crystal than in curve IZ resulting

in a analler dtsplecoment compared to the dark current curve,

However, the

uration value of the current of curve III is greater

than that of curve IT because more Light is absorbed in the todine

?ince the cut-off filter, CS 3-72, transmits 411 the long wavelengths

of the source which are absorbed in the iodine, and also there te less

Light absorbed in che ant!

ene. The cut-off ffiter ured for curve IV

cute off at a longer wavelength than that used for curve ITI, and taking

nto accounc che somctrai distribution of the eource explains the

relative porition of thts curve

Fig. 4 shovs the steady state apace charged Linited dark

current-voltage curves for a crystal before and after gamma irradiation.

?The parameter for these curver

8 the time of exposure to the game ray

source. It ts seen thet, after irradiation, the slope of the curve at low

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low current values is enaller chan at higher current values. For high

Arrattation Jones this slope at lov current values te two. This square

lav extends to larger

ages the longer the time the crystal is

srrads

fed, It {8 also seen that the saturation current, which ts

Aimost the same in all che curven, occurs at higher voltages chen

the {rradtation rine is longer. The curves in Fig. 5 were taken on

4 crystal which vas irradiated with gama rays for 3 hours. Curve 1

fe the dark current and curves IT, ITI and IV vere taken under t1-

lumination of intensity of 25, 50 and 100% respectively.

Fig. 6 shoes the x

welts of meagurenente caken on « crystal

after {radiating with x-raye. Ae Le seen the curves of Fig. 6 are

similar to those of Pig. 4.

SECTION V. THEORY OF SPACE CHARGE LIMITED CURRENTS

Te Ss well known that defects of solids produce changes in

the optical and electrical properties of solide. Thut the measurement

of these properties yields tnfornation about these defect states. Te

order co make crac:ical electrical meesurenencs in inevlatore one must

enhance the free carrier density. One way of doing this 4s by injecting

free carriers into the insulator. The current will then be Lintted by

the space charge injected into the crystal. The steady state current

for ideal crystals @iscussed by Mott and Gurney, (16) depends on

the square of the applied voltage and is inversely proportional to che

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cube of the crvatcl thickness. The theory of tne steady state spice

charge limited cucvent im veal crystels was given by Rose(*) and Lamperc?)),

Fron che nessuensu: of the SCL in crystals with traps ars dizcrace

energy level, the trap Censity and depth can be computed. Tho theary

the ©

fent apacy caarge Limited current for ths case of an des

crystal wes first piven by Many, Stehony, eter and Levinson? and independently by Helfrich and Markl?) the theory of the craneiont

United current for x

1 exystale vas given dy Many and

Prom transient measurements of the SCLC it ts possible

to compute the mobility and the trapping time of the carriers. There

results combined with those of the steady atate enables one to compuce

the capture cro

sction of the traps. Hence, the measurement of the

space charge limited current in {nsulators {ss powerful tool ta

determining che characteristics of defects. Since im thie report tie

Fesules of steady-state space charge Limit riven, e brie* review of the theory for the steady-ntace fn presented

below,

Following tespert derivation, che equations governing ¢:

steady stare current flow in a one dimensional plane geoweery crystal,

are the fotlowi

ta. y= gent) ea) gP fend) = constant

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Bq. 2

were 70) and "Uae in quast-aget librium.

?The J te the current density; £ is the electric field intensity; ee the mugnttude of the electric charge: { ta the electronic mobility; & fe the static dielectric constant of the insulator; D is che diffusion constant for electrons; "G)) and 7%(t) are the denaitien of the free sod trapped electrons respectively; and W and 7% are the values of 7 and My respectively in the bulk neutral crystal in thermal and electrical ?squiltbrtum, (chat 48, 20 applied voltage).

Tn solving these equations the diffusion tera in tq. 1 te steed, witch ta resoabie for voltages gratter chan AZ. 0.025 wots, ?The solution to hese equtions for the ideal crystal, (oo traps), with the voundary coudicton £= 0 at

wan given by Mott and Gurney by substi- tueing the expression for 7 in Bq. 2 into Bq. 1 and integrating with the above boundary condition. The result for J i etek

m3 Jefyeh

were Vso ne apttegvotage sat J te the expat

nlc.

Tampert gave the exact solution for 4 erysta] containing traps

ft eelnte ences Seat tor she cae are 2 ES 1 ere Bs i

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the trap level energy as measured fron the botton of the conduction band

.

and OF te the recat:

vel of the crystal at the anode. In this case the

current is diminished by a factor @ compared to the ideal case, (Bq. 3), cece AE ta the magne ofthe crap depth, andy andy are te

duaeeinn of mflable sates tn the coast on aad and rep reqetéon

im the current occurs and the value given by 8.3 for the ideal case ts

reached.

Lampert shoved that

current-voltage characteristics curves

ween plotted on a top T versus tog V plot wilt be contfned to Ite in «

a

erlangle as shown in Pig. 7. Por voltages lesa chan Vi the current

Will follow Ohm's Lav bectuse the cumber of injected carriers n(x) is 1 chan Fl , che mmber of Gerrans t=

absence of injection. For

a-0

voltages greater than V" in a trap free crystal, the current will

obey Child's Lav as given by Bq. 3. In the case of # real crystal the

departure from Oha's Lav will occur at # higher voltage due to the fact

that only & fraction of the total inject

carriers ts free. I? all the

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+12.

traps are at a single energy level the current vill again follow

av? ay but will be below the child's Law by a factor O

TEL

by Bq. 5. At the voltage, WV, when the mumber of injected carriers given

4s approximately equal to the number of tray

im the crystal, a large

rise {n the current occure for mall increases in voltage until the

child's Law value is reached. For higher voltages, since all the

traps are filled, the injected carriers

sn ideal cryetal and

child's Law 48 followed.

Yor crystals which contain trap levels that are distributed tn energy, 8 witt no longer be a constant but rather a function of

the voltage. Tn these cases, when the current departs from Oho? Law

Se will follow « voltage dependence T~ BU)V. one can see that

from a sinple steady state current-voltage measurement made on an

insulator with an injecting electrode @ large amount of information

can be ascertained. By taking the ratto of the experimental value

to the {deal Child's Law value for the current @ ie evaluated.

From the voltage dependence of O che energy distribution of the

ra

trap levels can be determined. Pron the Vo valve the trap density,

vgs ean be evaluated, tn che cane where Q 1a sor 4 foneton of the

voltage the energy depth of the craps can be found by vaing Eq. 5

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SECTION VE. concuusroNs

As {s seen im Fig. & the current-voltage curve is effected

by the gamma radiation in such a vay that for « given voltage the current

value is lovered. The larger the radiation dose, that te, going fram

curves TT to V, che lover 1s the current, There 1s also a change in

the slope. Beginning with curve IT the current at lov voltages departe

from av" dependence, where n> 2, to v? dependence. In curve Z

+ V eependence holds t111 the breakdom voltage. For Bigher radiation

doses the current are lover chan in curve F but the ¥? dependence still

holds.

These curves are interpreted in terms of che space charge Lintted

theory. Results simtlar to curve T, the measurements made on the thin

anthracene crystal before irradiation, have been reported by Mark and

nergeien(®). rhe

curves can be explained in cerms of an exponential

trap distrtbution. The lowering of the current value for a given voltage

going from curves IT to'Y, are interpreted in terms of traps which a

created by the radiation. Ae Ny, the density of craps Le incrat

a, the

munber of free carriers et a given voltage ts decreased. The gradual

change in the slope co a value of 2 for higher radiation doses strongly

Andicates that the traps introduced by the radiation are all at the same

Gtacrete energy level. Using the equations of the space charge Lintted

current theory outlined in Section V, the paraneters of these traps can

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- ue

¢ calculated. Fron curve IV of Pig. 4, the value of the voltage where

the curve departs from a equare law dependence is seen to be about 200 volts.

Taking this to be the vilue of the trapped filled limit voltage for the

aLh

TFL.

fnerodueed craps and using this valve tn the equation, Ve LEA

where L is the crystat thickness, J tho electronte charge, and ? the

Afelectric constant, Ne, che trap density, is calculated to be 2 x 10!3/em?.

From the ratio of the current of curve IV and the ideai ¥? curve, the ratio,

8, 18 % 10"

of states in che conduction band co be 10%4/en3, che vaiue of AL, the

Using Eq. 5 and, = 10!3/em? and taking Me, th umber

trap depth, 16 found to be 0.92 ev.

Prom curve 1 of Fig. 4 ir 4s seen that a saturation value of

the current { reached. as 1s seen frou curves IT and TET this saturation

value {8 not effected by the radiation, However, the voltage at which

curation occurs depends on the radiation dove, chat is on the number of

traps (ntroduced. The reason for chis ia that a8 the nuaber of traps ts

increased the mnber of free carriors 12 decronsed at any given voltage.

The electrode injection, which La the steady atete is dependent on the

number of free carrion

WINL in che case of greater trap density, hold

for higher voltages, Por the higher radlacton doces, curves TV and V,

4 breakdown occurs before the current saturation te achieved. In Fig. 5

the Light intensity dependence of the cusvent is shown for a crystal

where « large number of craps has been introduced. curve T of Fig. 5

was taken with a crystal in the dark, and curve TT was taken when the

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exyatel wes {Lluninaced by light which passed through filter C5 3-70,

(cut-off ar 4S00k"). Taking this Hehe intenetty as 100%, curves ITE

and 1V vere measured at {ntensittes of 50% and 25% respectively.

?The results taken on a crystal exposed to 120 kvp x-raye

4s shown in Fig. 6, ?The time of irradiation differs for each curve

?and vas adjusted so thar the total anocnt of energy absorbed in the

crystal was che sone as che equivalent curves for the gamma radiation

shomn tn Fig. 4. Te ts seen thet qualitatively and quantitatively the

curves are einglar.

ur work so far shove that anthracene crystals are damaged

by radiation fram gamma and x-rays and that this damage can be detect:

by electrical conductivity measurenents, This type of measurenent can

be used to measure the magnitude of the danage but doos not provide

information about the nature of the damage. we hope that the experiments

?we have planned for che future will enable us to obtain information

concerning the nature of the dé

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CURRENTCAMPS)

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?Typical park current-Voltage charactertatie

Curves for Different Todine Concentrations

0 1 . -

T- ELECTRODE USED 13 4 SATURATED

[> SQUTION OF 1ODINE iM Har

I- ELECTRODE 15 4 SATURATED

SOLUTION DILUTED 70 25%.

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vewaurs)

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CURRENTS CAMPS)

Fig. 3, current-voltage curve for @

and under Tilumtnation with

crystal in the Dark

Various Filters

T T ?T T

2 OAR

CORNING FILTER cog-7H

Pomel 3? 83-72

coon » C3370

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CURRENT CAMPS)

Fig. 4.

Derk Current-Voltages Curves of a Crystal

before and after Exposure to Gaama rays

for Different tines

T

roo

ENERGY ABSORBED /W THE CRYSTAL QUE

gL TO GAMMA /RRADATION

Z 60xi0 eres

I 2¢Xi0*ERGS

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E17 xiOF RCS

LeRYsra WeNsHT .0067 GRAMS

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MevOLTS)

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CURRENT (AMPS)

Fig. 5. cures

c-Volcage Curves

8 Function of Light

Intensity for a Crystal which vas Exposed £08

igh Carma ray Radiation Dose.

6

a en T ??T

ENERGY ABSORBED IN CRYSTAL DUE

70 GAMMA (RRADIATION 1S 2.7410" ERG

I DARK

Hl 25% Leu intensity

al. Bh 50% LsHT inreNsiTy |

| TE 100%.iGHT INTENSITY z,

si +

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Pig. 6. dark Current-Voltage Curves of « Crys!

and after exposure to woraye fer DLE

SP ATT

ENERGY ABSORBED INV CRYSTAL DUE

TO A-RAY IRRABIATION

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CHT 2185 GRAMS

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