

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. ---Page Break---  
[STUDY OF RADIATION DAMAGE IN ORGANIC CRYSTALS USING ELECTRICAL  
CONDUCTIVITY Salvador Cobas and H. Harry Szmant = Principal Investigators Progress Report  
#2 Work performed at Puerto Rico Nuclear Center Rio Piedras, P.R., under U.S. Atomic Energy  
Commission Contract T(40-1)-1833 (Project 14) March 1964 ---Page Break--- TABLE OF  
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Section III. Discussion of Radiation Damage Results 6 Section IV. Equipment ... 2 BADLMography .  
---Page Break--- 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 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. 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 the 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(?s3), 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  
---Page Break --- <2 recent developments such as the introduction of charge-injecting 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 a meaningful statistical interpretation it was necessary to produce  
our own crystals and for this reason we established a crystal growing station. In the 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 dichloroethane 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 fished out as soon as they attain an acceptable size. If the proper  
temperature gradient is not obtained the crystals 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 a second attempt to get good crystals because the xylene mixes slowly with  
the dichloroethane making a less dense solution in which it

It'll be more difficult to get the crystals to float our experience with the Kallmenn-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 spent weeks trying to grow crystals without

any success from a total of 150 crystals ranging in thickness from 10 to 70  $\mu\text{L}$  and from 0.3 to over 1 cm in area. Many of these crystals break in the process of being mounted in the Kallmann-Pope cell or develop a leak while undergoing measurements. We have tried to grow crystals using a modified Kallmann-Pope technique using 1,2-dichloroethylene instead of 1,2-dichloroethane, and cooling without covering the solution with xylene. The dichloroethylene has a relatively high density and the anthracene crystals float. After the crystals are fished out, they are cleaned with xylene to eliminate smaller debris from the surface of the larger crystals. Using this technique, we have grown 25 crystals. These 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 measurement. We have purchased from Harshaw Chemical Co. unselected anthracene crystals 10 mm x 10 mm x some which we have cleaved and polished to a 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 1 mm. We have made measurements on some of these crystals which are included in this report. SECTION ET. 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 unselected Harshaw crystals which we cleaved and polished to a thickness of approximately 200  $\mu\text{m}$  and on selected and polished Harshaw crystals of 300  $\mu\text{m}$  thickness. These measurements were done with the

Kelmann-Pope® cell using Wal-Nat, KacI-Mect, Na950, (NeT-Tp) electrodes and 36508 and 43604 Light. The measurements were done before and after irradiation with our one curie Pu+Be neutron source. The graph in Fig. 1 shows measurements done on our crystal #54 using the Mal-I electrode and Light of 4360A before and after irradiation with neutrons. The curve showing log  $\sigma$  versus log  $v$  after irradiation is incomplete 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 as high as one ampere. Fig. 2 shows measurements done on our crystal #143 before and after irradiation in which the values of  $\sigma$  after irradiation were measured with the Keithley Electrometer. Figs. 3, 4, and 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 #4-2(H) was cleaved and polished from a Harshaw unselected crystal and crystal #SH-1 selected and polished from a selected Harshaw 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>-Na,80, electrode and Light of 36504 before and after irradiation. The same measurements are shown in Fig. 6 of our Progress Summary Report No. 1. 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-I2 electrode and 43604 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 exalted conductivity returns gradually to normal pre-irradiation 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 species "activated" by the neutron irradiation and produced by the 43604 light source. The difference between "thin" and "thick" crystals can be explained in that little of the 43604 light fetches

the face of the crystal exposed to the iodine solution in the case of the "thick" crystal. Since anthracene is 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 a dislocation of a proton from anthracene, and the formation of transient anthracene carbocations and anthracene-proton complexes. The following is a calculation of the increase in ---Page Break--- the photocurrent that may be expected to be produced under our conditions of neutron irradiation and measurements by means of the iodine electrode. We mention that after exposing a crystal to our neutron source for approximately 70 hours, the crystal receives a dose of the order of  $3 \times 10^9$  n/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  $10^4$  atelocations per cm<sup>2</sup> were produced at the crystal surface after the 70 hour period of irradiation. Now, we shall consider the magnitude of the process to take place between the "excited" iodine 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  $10^{24}$ , it permits us to estimate that there are  $10^{24}$  iodine molecules/cm<sup>2</sup> at the surface of the anthracene crystal in contact with the 1M iodine.

solution. If the frequency of collisions between iodine and the anthracene crystals face is  $10^2$ /sec, then the number of collisions will be  $10^1$ /en?  $\times 10^2$ /sec or  $10^6$  collisions/sec cm<sup>2</sup>. A similar calculation following the procedure of Moelwyn-Hughes gives the number of  $10^0$  collisions/sec cm<sup>2</sup>, and that figure will be employed in the calculations which follow. If the cross section of capture of iodine by an "excited" anthracene is  $10^{7.5}$  cm<sup>2</sup>, then there is an area of  $10^4 \times 10^{7.5}$  or  $10^{7.1}$  cm<sup>2</sup> of "excited" anthracene at the surface, and the number of successful collisions between iodine and "excited" anthracene is given by  $10^0$  cm<sup>2</sup> (capture of  $10^{25}$  collisions/sec cm<sup>2</sup> or  $10^{14}$  collisions/sec). Should each such collision produce an additional carrier, then the resulting current would be  $10^{14} \times 1.6 \times 10^{-19}$  coulombs/sec cm<sup>2</sup> =  $1.6 \times 10^{75}$  emps/cm<sup>2</sup>. In a crystal of 0.1 cm<sup>2</sup> surface, this results in a current of  $1.6 \times 10^0$  amps. This indeed is the magnitude of the "excited" current which is indeed observed. The effect of photoactivation on the iodine - "excited" anthracene intersection 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 equation is "SAL" and letting  $2 \times 10^{-3}$  cm/ a c be the diffusion constant =  $L e a t / \text{acc.}$  the value of the jump length  $L = IDE$  where 12 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 around  $10^{-2}$  cm and the jump time is  $10^{-7}$  sec. We now estimate the

transit time of carrier in 4 10 mlorgn thick anthracene crystal when we apply 4 volts to ve  $Ce = x LO$  ot so wots wove Os  $A = 2 ye$  an iodine molecule with a jump time of  $10^0$  sec =  $3 \times 10\%$  Therefore in the interval of  $10^8$  produces  $10^?$  jumps. If we place a given iodine molecule at  $10^0$  ca from the surface, it will probably hit the surface at least once during an ---Page Break--- "9 interval of time equal to the transit time. This then,  $10^0$  om, 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  $10^0$  for 1 M iodine, 6 vex Ledn fF oh  $x1 w = 107^0$  and  $Vig = 1 = 0.9$  Thus 10% of the light is absorbed, and with a light intensity of  $10^4$  quanta/en?/sec there will be  $10^?$  "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 4360 Å 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 4360Å 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 occurrence of electron transfer which produces iodide radicals, so  $\epsilon_a \approx 4.9$ :  
---Page Break--- =o - 'This process represents a hole injection mechanism which is more favorable than that which probably occurs in the dark,  $\epsilon_a \approx 4.9$  for which occurs when the anthracene has not been exposed to neutrons,  $\epsilon_a \approx 4.9$  (process in the dark)  $\epsilon_a \approx 4.9$  (process under illumination) In the anthracene crystals containing

dislocated protons, thermal activation will eventually cause the return of the protons to the anhydride! carbocations: (84:4) 4 4:  $\epsilon_a \approx 4.9$  and  $\epsilon_a \approx 4.9$  explains the gradual loss of the enhancement in the saturation current. An alternate explanation of the effect of the 4360Å 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. ( $\epsilon_a \approx 4.9$ ) and ( $\epsilon_a \approx 4.9$ ) will be promoted by the absorption of light to the polar spectra ( $\epsilon_a \approx 4.9$ ) and ( $\epsilon_a \approx 4.9$ ) then initiate a chain of electron transfer within the anthracene. Both kinds of charge-transfer complexes  $\epsilon_a \approx 4.9$  respectively, on the power crystal. ---Page Break--- 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 a vacuum system to repurify the anthracene we obtain from commercial sources. We have a Fisher Scientific zone refiner to further 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, 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 measurements (Fig. 9) and other optical pulse transient photoconductivity measurements. (Fig. 10). The equipment for steady voltage has already been tested and is ready to be used for transient photoconductivity 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. ---Page Break--- oe  
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