

LETTERS TO THE EDITORS

PHYSICS

Surface-controlled Bulk Conductivity in Organic Crystals

In an earlier paper¹ experiments were described which demonstrated hole injection from unexcited and optically excited electrode layers into an adjacent anthracene crystal, resulting in a large increase in the current passing through the bulk of the crystal. In the present communication, the interaction between an optically excited anthracene crystal and its adjacent electrode is reported.

The experimental techniques used have been described in detail elsewhere^{2,3}. The general procedure was to use an electrolyte as the electrodes for thin (10 μ) single crystals of anthracene. The incident light passed through the electrolyte before striking the crystal face. The current through the crystal was measured with 1M sodium iodide and 1M sodium chloride solutions in contact with the illuminated side of the crystal, using 3650 Å. light which was transmitted by the electrolyte but completely absorbed by the anthracene.

at least part of the current measured with the illuminated side negative is due to an interaction at the unilluminated electrode which produces positive holes at that face. The total i^- current would, therefore, be made up of the flow of these holes from the face not directly illuminated as well as electrons from the illuminated face. On this basis, the flow of electrons in i^- in the case shown in column 6 must be less than 0.3 per cent of i^+ .

In all cases, the photocurrents were almost saturated at 50 V. or lower. The dark current did not exhibit saturation.

The quantum efficiency for the photocurrent when the illuminated face of the crystal was in contact with sodium chloride solution was one carrier liberated into the anthracene crystal for thirty quanta falling on the face of the anthracene. In the case where the illuminated face was in contact with sodium iodide solution, the quantum efficiency was one carrier liberated into the anthracene for 390 quanta falling on the face of the anthracene.

In general, these results may be understood by assuming that the observed photocurrents are a

Table 1. PHOTOCONDUCTIVITY IN ANTHRACENE USING SODIUM CHLORIDE AND SODIUM IODIDE ELECTROLYTE ELECTRODES

Applied voltage (Volts)	(1) Side A: NaI B: NaI Dark current	(2) A: NaI B: NaCl Dark current		(3) A: NaI B: NaI Photocurrent		(4) A: NaI B: NaCl Photocurrent		(5) B: NaI A: NaI Photocurrent		(6) B: NaCl A: NaI Photocurrent	
	$i^+ = i^-$ *	i^+	i^-	i^+	i^-	i^+	i^-	i^+	i^-	i^+	i^-
	$\times 10^{13}$ amp.	$\times 10^{13}$ amp.		$\times 10^{14}$ amp.		$\times 10^{14}$ amp.		$\times 10^{14}$ amp.		$\times 10^{14}$ amp.	
2				10	0.33	6.5	2.1	4.1	0.40	13.6	0.25
4	0.3	0.2		21	0.40	14.5	3.5	11.5	0.52	41.6	0.40
8	0.5	0.5		29	0.46	22.5	4.3	17.5	0.63	148	0.60
15	0.9	1.1		36	0.52	29	4.5	21.5	0.72	240	0.80
30	1.7	2.5	3.5	40	0.58	33	4.7	24.0	0.81	312	1.05
50	3.0	4.4	6.0	42	0.62	35	5.0	25.2	0.87	328	1.15

Area of crystal, 0.1 cm.². Intensity of 3650 Å. light, 320 μ watt/cm.². All solutions are 1M in concentration.

* i^+ and i^- refer to currents measured when the polarity of the side illuminated by light was positive and negative respectively.

† Note change in scale.

The side illuminated by the light is listed at the top of each column in the table.

The experimental results are given in Table 1. The most interesting result was that the magnitude of i^+ when the illuminated side of the anthracene was in contact with sodium chloride solution (column 6) was 13 times that of i^+ when this side was in contact with sodium iodide solution (column 5). The current i^- did not change much.

It was also noted that the ratio i^+/i^- in the case shown in column 6 was 285 as compared with a ratio of 7 in the case shown in column 4. The large value of i^- in column 4 was felt to be due in most part to an effect of fluorescent light on the anthracene-sodium chloride electrode face not directly illuminated. Scattering effects were ruled out by shielding the unilluminated face. Using identical sodium iodide electrodes, the ratio i^+/i^- at 50 V. was 68 (column 3). The latter experiment was repeated with no change other than shifting the illumination from one face of the crystal to the opposite face. The ratio i^+/i^- was 29 (column 5), indicating some crystal asymmetry. The change from sodium chloride to sodium iodide in the electrolyte at the unilluminated side decreases the i^- current, however, by a factor of 8, whereas the i^+ current is almost unchanged (compare columns 3 and 4).

This dependence of i^- on the nature of the electrolyte in contact with the crystal face indicates that

result of the creation of an exciton by the light absorbed in the anthracene and its subsequent diffusion to the adjacent electrode, where it undergoes a dissociation into an electron and a positive hole. The latter then moves through the anthracene under the action of the electric field. Any event which will quench the exciton or inhibit its subsequent dissociation will diminish the photocurrent. Apparently such quenching occurs at the electrode by the I⁻ and its quenching action is greater than that of the Cl⁻.

A more complete discussion of these results will be given shortly.

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¹ Kallmann, H., and Pope, M., *J. Chem. Phys.*, **32**, 300 (1960).

² Kallmann, H., and Pope, M., *Rev. Sci. Instr.*, **29**, 993 (1958).

³ Kallmann, H., and Pope, M., *Rev. Sci. Instr.*, **30**, 44 (1956).