998. *Photo- and Semi-conductance of Organic Crystals. Part VI.* Effect of Oxygen on the Surface Photo-current and Some Photochemical Properties of Solid Anthracene.*

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The photocurrent, I_s, in anthracene mounted in a surface cell was shown to be proportional to the amount of oxygen adsorbed on the surface. The heat of adsorption of oxygen was found to be 5 kcal./mole. Evidence was obtained consistent with the double-layer theory of the oxygen effect both in air and in a vacuum. Some photochemical properties of anthracene crystals in air were examined. In the presence of oxygen small amounts of anthracene peroxide and anthraquinone were measured. The formation of anthraquinone was responsible for the fact that, in air, I_s increased with temperature at first and then decreased.

Photo-conductance in anthracene [1] varies with the presence of oxygen in the surrounding atmosphere, and this is especially true of the surface photo-current I_s, *i.e.*, the current observed in a cell with the electrodes on the one surface of the crystal. The present work reports quantitatively the dependence of the surface photocurrent on oxygen pressure, the amounts of compounds of anthracene with oxygen formed under the action of light, and related questions. Certain results have been summarized in preliminary reports.[2]

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* Part V, *J.*, 1957, 5001.

[1] Part I, Bree, Carswell, and Lyons, *J.*, 1955, 1728.
[2] Bree and Lyons, *J. Chem. Phys.*, 1956, **25**, 384, 1284.

EXPERIMENTAL

The experimental procedure for measuring I_s was similar to that described previously.[1] A variety of evacuable cells were designed to fit directly to a compact amplifier built from a 956 acorn-type valve connected in a well-known electrometer circuit.[3]

Effect on I_s *of varying the Oxygen Pressure.*—The variation of I_s with oxygen pressure, p, was reversible; I_s varied non-linearly with p. However, the plot of p against p/I_s was linear for oxygen pressures greater than 10 mm. (Fig. 1). A graph of log I_s against log p was also linear over an intermediate pressure range. This marked similarity to a Langmuir adsorption isotherm, in the first case, and to a Freundlich adsorption isotherm, in the second, suggests that a monolayer of oxygen is adsorbed on the crystal surface and that I_s is proportional to the amount of oxygen adsorbed.

At low pressures (continuous pumping at 10^{-5} mm. of mercury) and at elevated temperatures, sublimation of anthracene was noticeable. When the cell was not in a thermostat a fine white powder slowly settled on its inner walls and on those surfaces of the crystal which were not illuminated. In the jacketed cell, used at higher temperatures, anthracene condensed on the cooler, upper portion, but the crystal surface facing the light remained clear. The useful pressure range became more limited as the temperature was increased.

In order to compare readings for a number of crystals on the same graph, I_s observed at pressure p was expressed as a fraction of the photocurrent, $I_{\text{max.}}$, when the surface was saturated with adsorbed oxygen. It follows from Fig. 1 that oxygen was partially desorbed at higher temperatures; *e.g.*, with an oxygen pressure of 160 mm. (*i.e.*, a pressure of air of one atmosphere), the surface was 95% covered at 25°, 90% at 50°, 86% at 70°, and 82% at 90°. By prolonged irradiation, the vacuum photocurrent was reduced to 2—3% of the value in air at room temperature.

The use of air in place of pure oxygen gave results which indicated that nitrogen is not adsorbed on the crystal surface and that I_s depended on the partial pressure of oxygen.

Readings were recorded on twelve crystals whose thicknesses ranged from several microns to about 1 mm. The photocurrent in every crystal examined in this way showed a similar dependence on the oxygen pressure. All the crystals mounted in this series of experiments gave I_s values of the same order of magnitude although, in general, the thicker samples, cleaved from a single crystal supplied for use as a scintillation counter, exhibited a smaller photocurrent than the thinner sublimation flakes. The error in mounting crystals in a reproducible manner was lessened by using a fixed inter-electrode distance of about 2·5 mm., and constant applied voltage and light intensity.

Inokuchi [4] has reported that oxygen does not increase the photocurrent in anthracene single crystals at 90°. This conclusion appears to contradict the result found in this work (see Fig. 1), but a possible explanation arises from the different methods of crystal mounting. In our work, the electrical contacts were made on the same crystal face (surface cell), while Inokuchi applied the electrodes to opposite crystal faces (sandwich cell). Previous workers have shown that in a surface cell the current is carried in a surface layer and that in a sandwich cell only a very small surface conductance is observed.[5]

From graphs of log p against $1/T$ (where T is the absolute temperature of the crystal) for constant amounts, θ, of adsorbed oxygen, estimates of the heat of adsorption were made (Fig. 2). At pressures greater than 10 mm., the heat of oxygen adsorption given by $(-\boldsymbol{R} \ln p)/(1/T)$ for constant θ was (5 ± 2) kcal./mole.

Double-layer Experiments.—Two possibilities have been considered by various workers [6,7] to account for the influence of oxygen: (*a*) a participation by the oxygen in the formation of charge carriers, a process which conceivably could, but need not, involve the formation of new chemical species (*e.g.*, an oxy-compound or the triplet state of anthracene molecules); and (*b*) a modification by oxygen of the properties of the electrical double layer assumed to exist at the crystal surface. We therefore studied the effects, both in air and in a vacuum, on I_s

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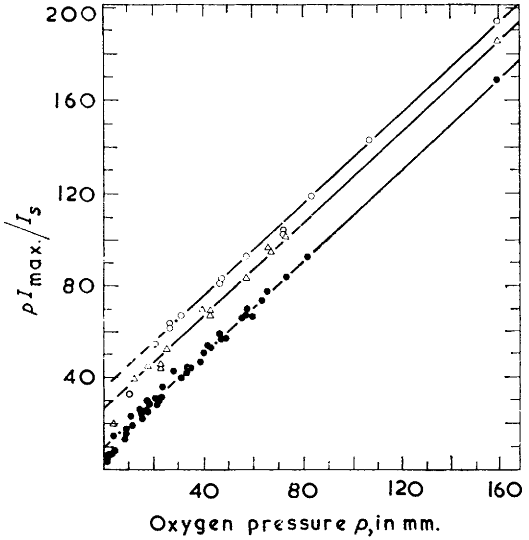
[3] Hughes, *Electronic Eng.*, 1951, **23**, 217.
[4] Inokuchi, *Bull. Chem. Soc. Japan*, 1956, **29**, 131.
[5] Compton, Schneider, and Waddington, *J. Chem. Phys.*, 1957, **27**, 160.
[6] Lyons, *J. Chem. Phys.*, 1955, **23**, 220.
[7] Schneider and Waddington, *J. Chem. Phys.*, 1956, **25**, 358.

of electrically induced double layers.[8] Schneider *et al.*[5] about the same time did similar experiments in an inert atmosphere and our results agree with theirs. A charge was placed by means of a high-tension D.C. supply on a copper disc brought close and parallel to the crystal surface.

In a vacuum, the photocurrent increased when the copper disc was made more negative than the crystal, and decreased when the disc was more positive. This indicated that any charge associated with an adsorbed oxygen layer was negative in sign. There was a prompt response of the photocurrent to any change in the induced charge on the " condenser " plates and, over the range of potential difference applied, the photocurrent variation was proportional to the strength of the field between the plates.

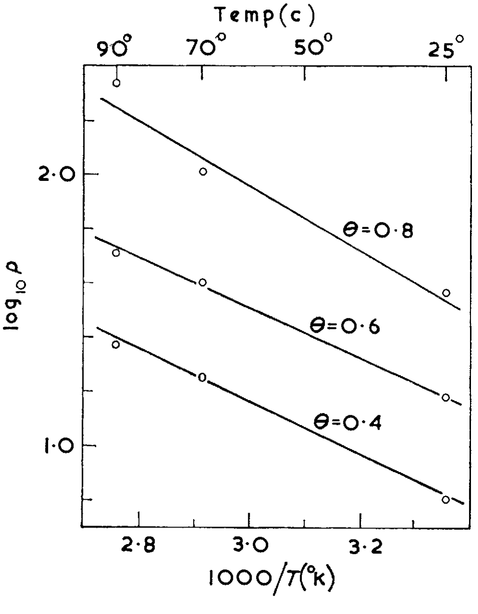
The use of high potentials across the " condenser " plates was restricted by the occurrence of a discharge which depended on the gas pressure and the applied field. Bombardment of the crystal with charged particles of either sign, caused by holding the potential difference across the " condenser " slightly lower than that needed to cause a discharge, very much reduced the photo-conductance. Bombardment for periods of less than 1 min. decreased the crystal sensitivity by as much as 75%. A small part of the sensitivity (about 10%) was slowly recovered during some hours.

FIG. 1. *Test of the applicability of a Langmuir isotherm.*



○, △, ●, refer to different crystals.

FIG. 2. *Graphs for estimating the heat of adsorption: θ is the fraction of the surface which is covered by oxygen.*



In air the time of response of the photo-conductance to the modulating field increased very much (see Fig. 3). With the copper disc charged negatively, there was a marked increase in the photocurrent followed by a slow decrease to the initial value; with a positive charge on the copper disc, the photocurrent sharply dropped to about half the initial value and then slowly increased. The final equilibrium photocurrents, recorded after about 2 hr., were identical with the initial readings irrespective of whether the copper disc was charged positively or negatively.

The results of the double-layer experiments are therefore consistent with the idea that the effect on I_s of oxygen and other gases is through a modification of a surface double layer. The exact nature of the charged species remains uncertain. The differing behaviour in air and in a vacuum seems consistent with the relative difficulties of altering a double layer which is already well established by adsorbed oxygen.

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[8] See, *e.g.*, Shockley, " Electrons and Holes in Semiconductors," van Nostrand, New York, 1950, p. 29.

Time Effects.—The time required for the anthracene–oxygen system to attain equilibrium depended on the intensity, L, of light incident on the crystal surface; equilibrium was reached more quickly as L was increased. With a 125 w high-pressure mercury arc placed 5 cm. from the crystal, equilibrium was established in about 60 min. The time constant of the apparatus itself was less than 1 min. For the low fields used here, equilibration was independent of the applied field strength, E. The system thus arrives at equilibrium through a stage involving an activation energy. Equilibrium may be visualized as a particular distribution of charge in a direction normal to the crystal surface. The attainment of equilibrium is assisted, therefore, by a higher rate of formation of charges and this in turn increases with the light intensity. Thus it is possible to understand the time effects in terms of electrical double layers.

Variation of I_s *with Temperature,* T.—In air, I_s varied irreversibly with T; I_s first increased with T, as shown by the curve AB in Fig. 4. A further increase of temperature caused I_s to decrease along BC, and then lowering the temperature brought about the decrease from C to D. The I_s–T curve was reversible along DC for all temperatures less than the maximum (T_C) reached in the preliminary treatment, although, if the crystal temperature was held at values near T_C, there was a slow decrease in I_s. The value of T_B, the temperature at which I_s reached a maximum on the curve AC (Fig. 4) varied from crystal to crystal; T_B was about 90°, when a cleaved portion of a scintillation counter was used, whilst a value of about 60° was obtained with a number of very pure, thin sublimation flakes.

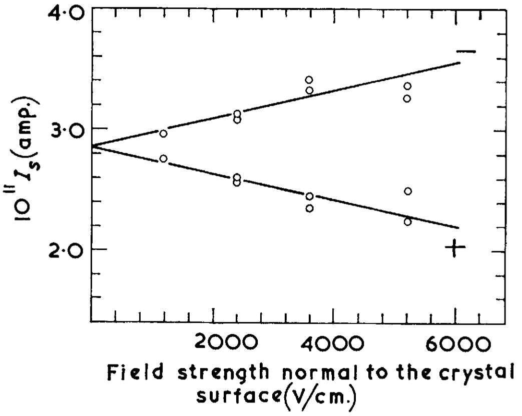


FIG. 3. *The effect on I_s of a field normal to the surface of the crystal. The sign of the metal electrode is shown.*

An activation energy, b, calculated from the reversible portion (DC in Fig. 4) of the I_s–T curve by using the formula $I_s = a\,[\exp(-b/kT)]$ was (0·20 ± 0·05) ev, the mean of a number of measurements on six crystals. The activation energy of this photoconductance process was also (0·20 ± 0·05) ev, from measurements of I_s as a function of T before heating above 50°. This estimate also was made from measurements on six different crystals.

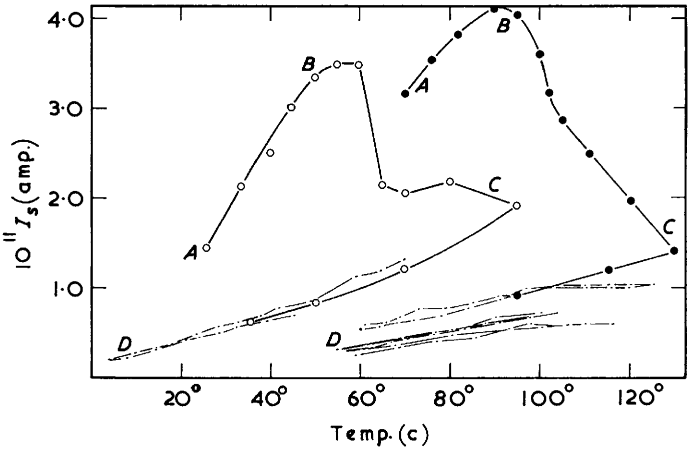
The occurrence of a maximum in the curve ABC may be understood if there is formed at elevated temperatures a layer of a compound of oxygen with anthracene. This layer then prevents the usual promotion of I_s by oxygen by preventing the usual effect on the double layer. The layer responsible is most likely to be anthraquinone (see below). Another explanation altogether has been suggested [9] to explain the maximum in the curve ABC. Sublimation was assumed responsible. The incident-light intensity was thought to be reduced by the presence of anthracene vapour between the crystal and the cell wall and also by the condensation of anthracene powder on the cell wall. However, light absorption by anthracene vapour is much too weak to explain the observed peak. The results shown in Fig. 4 were obtained by using the jacketed cell. Heat supplied by the hot liquid which circulated through the glass jacket was conducted by gas molecules from the hot inner glass wall to the crystal. Sublimation occurred at elevated temperatures and a white anthracene powder was slowly formed on the upper unheated portion of the cell. The exciting radiation was directed on to the crystal through the hot circulating liquid and the heated glass walls. Thus no anthracene condensed on the hot glass wall and so the incident light was not absorbed in this way.

[9] Rosenberg, personal communication.

The influence of the crystal surface on I_s being so great, the chemical nature of the surface was investigated.

Photo-formation of Anthraquinone.—Anthracene crystals irradiated in air above 60° became coated with a yellow material on the irradiated surface. This effect was much less evident after long irradiation at room temperature, than above 60°. The yellow surface compound was identified as anthraquinone by three tests: (*a*) A deep red coloration in alkaline aqueous alcohol containing zinc dust. (*b*) Absorption (in EtOH) from 5000 to 4400 Å (see Table 1); the amount of anthraquinone formed on the surface at room temperature increased with the time of irradiation. (*c*) Polarograms (Fig. 5) of the coloured crystals and of anthraquinone, both showing a half-wave potential at −0·40 v referred to a saturated calomel electrode in an aqueous dioxan solution of pH 5·6.

FIG. 4. *The dependence of* I_s *upon temperature, in air.*



○ *Thin flake.* ● *Crystal* 1 *mm. thick.*

Formation of Anthraquinone from Anthracene Peroxide.—Anthracene peroxide was unstable both in solution and in the solid form at room temperature. Anthraquinone was identified spectroscopically as one decomposition product. Absorption peaks (in EtOH) common to pure anthraquinone and solid anthracene peroxide stored for 3 months at room temperature occurred at 2530, 2720, and 3300 Å (infl.); an anthracene peroxide solution, stored for 3 days had peaks at 2540, 2720 (infl.), and 3280 Å in EtOH and at 3330, 3200, and 2700 Å in hexane. Anthracene was not detected as a decomposition product. Anthracene peroxide decomposed more rapidly in solution than as a solid. Light accelerated the decompositions, yet peroxide solutions stored in complete darkness yielded a detectable amount of anthraquinone at room temperature within a day.

TABLE 1. *The optical density* (×10³) *of the anthraquinone formed at the surface of* 0·100 *g. of irradiated anthracene crystals.*

(The exposed anthracene crystals were dissolved in 5 ml. of an ethanol–carbon disulphide solution of glacial acetic acid; this solvent [10] was also used in the reference cell. The path length of the solution was 2 cm. The average thickness of crystals was about 20 μ.)

Time of exposure:	5 min.	5 min.	15 min.	1 hr.	1 hr.	2 hr.	5 hr.	7 hr.	7 hr.
λ (Å)									
5000	2·5	4	9	9	5	10	17	24	25
4900	2·5	4	9	10	5	12	19	27	28
4800	2·5	4	9	10	6	13	23	33	34
4700	3	4	9	12	6	17	28	40	42
4600	3	5	10	14	6	22	35	50	50
4500	4	5	10	17	6	27	42	15	60
4400	5	5	13	22	7	33	50	72	72

Polarographic evidence also indicated that the peroxide decomposed both as a solid and in solution (see Fig. 5). The half-wave potential of the peroxide measured with respect to the saturated calomel electrode was almost zero and was strongly pH-dependent. At pH 7·0 and 5·6, the half-wave potential was at —0·003 and about +0·30 v, respectively. The polarograms in Fig. 5 show that the decomposition yielded at least one intermediate product with a half-wave potential of —0·104 v at pH 5·6. However, the height of the wave at —0·104 v slowly decreased during a period of hours and the anthraquinone wave at —0·40 v (pH 5·6) appeared. The polarogram of some solid peroxide kept at room temperature for 3 months is also shown in Fig. 5 (curve 4). The reduction waves, therefore, show the presence of the peroxide, the quinone, and the unstable intermediate.

Photo-formation of Anthracene Peroxide.—From kinetic studies, Bowen and Tanner [10] concluded that the formation of anthracene peroxide in solution is initiated by anthracene molecules in triplet states. Evans [11] has recently shown that the presence of oxygen in an anthracene solution relaxes the symmetry rules that forbid the appearance of singlet–triplet electronic transitions, so that these transitions appear with increased intensity. At the surface of an anthracene crystal, adsorbed oxygen molecules are close to anthracene molecules. Mixing of the anthracene singlet and triplet levels should again occur, so that the probability of populating the lowest anthracene triplet level should be increased. For this reason a search was made for anthracene peroxide on the illuminated surfaces of anthracene crystals stored in oxygen.

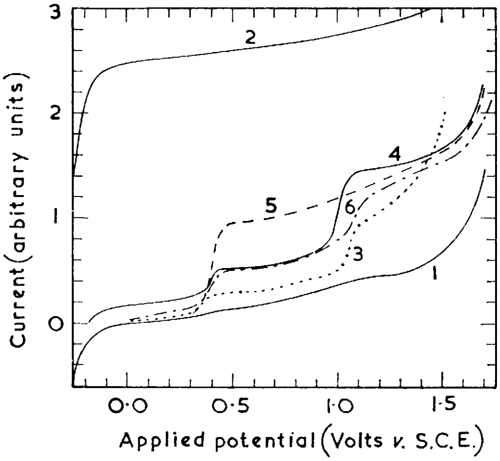


FIG. 5. *Polarograms of some anthracene derivatives*: (1) *Blank run on the solvent*; (2) *fresh solution of pure anthracene peroxide*; (3) *solution* (2) *after storage*; (4) *fresh solution of a sample of anthracene peroxide which had been stored for* 3 *months*; (5) *pure anthraquinone*; (6) *anthracene crystals after exposure in air to ultraviolet light.*

Anthracene crystals about 20 μ thick, which were obtained by sublimation in nitrogen, were exposed in air to the light from a mercury lamp. The exposure time was varied. The crystals after irradiation were analysed quantitatively for anthracene peroxide by comparing the results from various crystal batches with those from pure peroxide samples [10] treated in the same way.

One method of analysis estimated spectrophotometrically the amount of iodine liberated by the peroxide in carbon disulphide from an alcoholic solution of potassium iodide and acetic acid.[10] Since anthraquinone is formed on the crystal surface on prolonged irradiation, and iodine and anthraquinone both absorb light of wavelengths between 5000 and 4000 Å, it was necessary to estimate the amount of anthraquinone before the alcoholic potassium iodide solution was added: the amount of the peroxide present was calculated from the difference in the absorption before and after the addition of the iodide solution.

The results of the estimations of the peroxide are summarized in Table 2. All measurements were carried out with cells of 2 cm. length in a Uvispek spectrometer. The concentration of exposed anthracene crystals in the solution is quoted for each series of measurements. Readings at wavelengths below 4300 Å were disregarded since absorption is expected there by the very strong solutions of anthracene. Because the peroxide concentration was at the

[10] Bowen and Tanner, *Trans. Faraday Soc.*, 1955, **51**, 475.
[11] Evans, *J.*, 1957, 1351.

limit of detection, a large number of readings were made under different conditions; the time of exposure was increased until the crystals were noticeably yellow (anthraquinone absorption then interfered) and the concentration of exposed crystals was increased beyond the limit of solubility with the excess filtered off. Scrupulous care was taken in cleaning the cell end-plates and in setting the cell in its compartment in a reproducible manner. However, since any error arising from this source would be constant over the spectral region used, it was eliminated by taking the optical density reading at the longest wavelength as a reference point and subtracting this value from the optical densities observed at the lower wavelengths. The adjusted optical densities are shown in the Tables and are proportional to the concentration of iodine.

TABLE 2. *The optical density* ($\times 10^3$) *of iodine liberated by the peroxide formed at the surface of irradiated anthracene crystals after correction for the anthraquinone formed simultaneously.*

Time of exposure:	0			5 min.			15 min.	1 hr.			2 hr.				3 hr.	5 hr.	7 hr.	9 hr.
λ (Å)																		
5000	2	−1	0	8	5	−1	0	4	2	6	1	7	−1	3	2	7	7	8
4900	2	−1	0	9	5	0	0	5	4	6	1	9	6	3	2	6	10	9
4800	2	0	0	10	5	0	0	5	4	7	1	10	10	4	1	6	10	10
4700	2	1	0	11	5	2	0	4	6	6	1	11	23	5	2	5	9	8
4600	2	4	0	13	5	4	0	4	6	6	1	12	37	5	3	3	10	9
4500	1	5	0	12	5	6	2	5	9	8	1	15	50	7	0	5	12	13
4400	1	5	0	13	5	6	1	4	8	9	0	17	62	8	3	6	15	13
Wt. of crystals*	25	30	13	13	29	29	10	10	30	12	13	141	90	88	71	12	13	12

* This weight (mg.) of exposed anthracene crystals was dissolved in 5 ml. of an ethanol–carbon disulphide solution, potassium iodide, and glacial acetic acid.[10] The path length of the solution was 2 cm.

The optical densities although small are significantly positive; only two of the 105 readings were negative. It may be concluded, then, that anthracene peroxide is formed at the surface of anthracene crystals.

A solution of pure anthracene peroxide at a concentration 0·1 mg./10 ml., treated in a similar way, gave optical density values for the iodine absorption of 0·074 at 5000, 0·102 at 4900, 0·136 at 4800, 0·182 at 4700, 0·240 at 4600, 0·316 at 4500, 0·424 at 4400, 0·578 at 4300, and 0·752 at 4200 Å. These values are the means of three sets of readings. From them it was deduced that at most only about two molecular layers at the surface of irradiated anthracene crystals are converted into the peroxide. On crystals not irradiated an almost negligible amount of peroxide was detectable.

The height of the reduction wave in polarographic measurements confirmed the presence of anthracene peroxide. This method was not exhaustively studied, for the concentration of the peroxide present on the crystal surface again was at the limit of detection. However, the polarogram taken on exposed crystals (curve 6 of Fig. 5) showed (i) that there was a small increase of the wave height at zero potential where the anthracene peroxide wave was expected. The increase was about twice the magnitude of the error involved in reproducing the results and is thus significant. The wave height corresponded to the conversion of about three molecular layers of the anthracene crystal into the peroxide. Also (ii) the anthraquinone wave appeared at −0·40 v, and (iii) a wave appeared at about −1·0 v. Most significantly, this wave appeared at about the same reduction potential (−1·0 v) as was expected for the intermediate product in the decomposition of the peroxide to the quinone. This observation supports the conclusions that some peroxide was formed at the irradiated crystal surface and that the peroxide decomposed to the quinone through an intermediate. The quinone observed on the irradiated crystal surface therefore may be formed *via* the peroxide.

Photo-conductance of the Photochemical Products.—Anthracene peroxide and anthraquinone were tested for photo-conductance by using an amplifier which could detect 10^{-16} amp.

Anthraquinone crystals were grown from aqueous alcohol as long needles. A number of these crystals was mounted across the electrodes by using " Aquadag " after it was ascertained by observation under a polarizing microscope that all were single crystals. No photocurrent could be detected even when the applied field strength was increased to 3000 v/cm. and the light intensity was increased to a maximum. In this experiment, the mercury lines were separately directed on to the crystal, but no wavelength down to 2537 Å was effective in exciting a measurable photocurrent.

No large single crystals of anthracene peroxide could be grown by recrystallization. Sublimation methods and growth from the melt were obviously not appropriate. However, a multicrystalline mass, formed by pressing the product firmly on to the filter-paper during the final recrystallization, was used. Again no photocurrent was observed even in the low wavelength region (less than 2500 Å) where, from a consideration of the solution spectrum,[12] the solid sample was expected to absorb.

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[12] Gillet, *Bull. Soc. chim. France*, 1950, 1135.