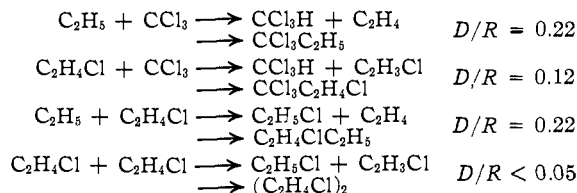


and relates $R_{C_2H_5Cl}$ to $R_{(C_2H_4Cl)_2}$ and $R^{1/2}C_4H_{10}$

$$\frac{R_{C_2H_5Cl}}{R_{(C_2H_4Cl)_2}} = \frac{k_5}{k_3} + \frac{k_{14}}{k_3^{1/2}k_{10}^{1/2}} \frac{R^{1/2}C_4H_{10}}{R^{1/2}(C_2H_4Cl)_2} \quad (V)$$

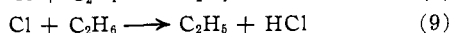
Equation V is plotted in Fig. 2 for the data obtained at 0, 30 and 58°. Again no temperature effect is visible. From Fig. 2 we obtain $k_2/k_3 \leq 0.05$ and $k_{14}/k_3^{1/2}k_{10}^{1/2} = 0.42 \pm 0.03$. Previous estimates indicated $k_5/k_3 \leq 0.1$.³ No data are available in the literature for $k_{14}/k_3^{1/2}k_{10}^{1/2}$. Accepting $k_{12}/k_3^{1/2}k_{10}^{1/2} = 1.92$ ⁸ we calculate $k_{12}/k_{14} = 0.22$.

It is interesting to compare the various ratios of rate constants for disproportionation over recombination (D/R) obtained in this investigation



The ratio of disproportionation over recombination for two ethyl radicals is 0.14 ± 0.02 .¹⁰⁻¹² The results clearly indicate that the substitution of one or more ethyl radicals by chlorinated alkyl radicals has a considerable effect on the ratio of disproportionation over recombination. The number of hydrogen atoms available for disproportionation seems to have little or no relation to the observed ratios.

Finally, we have attempted to measure the activation energy difference between reactions 2 and 9



According to these reactions $R_{C_2H_4Cl}/R_{C_2H_5}(C_2H_6)/[C_2H_4] = k_2/k_9$. In the above equation $R_{C_2H_4Cl}$ denotes the rate of production of C_2H_4Cl radicals, $R_{C_2H_5}$ the rate of production of ethyl radicals. Approximate values for $R_{C_2H_4Cl}$ and $R_{C_2H_5}$ may be calculated from $R_{C_2H_4Cl} = 2R_{(C_2H_4Cl)_2} + R_{C_2H_3Cl} + R_{CCl_3C_2H_4Cl} + R_{C_2H_5Cl} + 0.12R_{CCl_3C_2H_4Cl}$ (to account for C_2H_5Cl pro-

(10) R. K. Brinton and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1840 (1955).

(11) D. G. L. James and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A244**, 289 (1958).

(12) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1062 (1955).

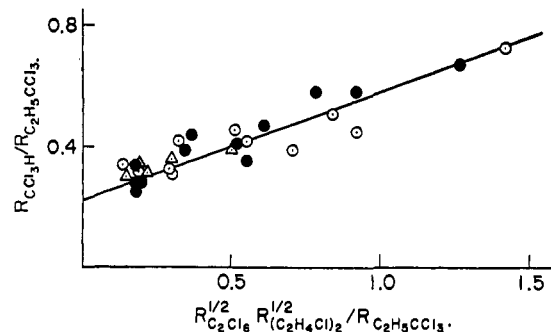


Fig. 1.—Plot of $R_{CCl_3H}/R_{C_2H_5CCl_3}$ vs. $R^{1/2}C_2Cl_6 R^{1/2}(C_2H_4Cl)_2 / R_{C_2H_5CCl_3}$ at 0° (●), 30° (○) and at 58° (△).

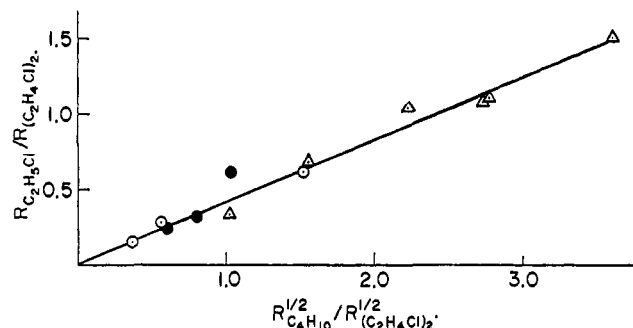


Fig. 2.—Plot of $R_{C_2H_5Cl}/R_{(C_2H_4Cl)_2}$ vs. $R^{1/2}C_4H_{10}/R^{1/2}(C_2H_4Cl)_2$ at 0° (●), 30° (○) and 58° (△).

duced by reaction 8) and $R_{C_2H_5} = 2R_{C_4H_{10}} + 0.28R_{C_4H_{10}}$ (to account for C_2H_6 and C_2H_4 production by reaction 11) + $R_{C_2H_5Cl} + 0.22R_{C_2H_5Cl}$ (= $R_{C_2H_5}$ produced by reaction 14) + $R_{C_2H_5CCl_3} + 0.22R_{C_2H_5CCl_3}$ (= $R_{C_2H_5}$ produced by reaction 16). Data thus obtained for k_2/k_9 are given in Table I for all runs where we were able to measure C_2H_5Cl production. It is obvious that this method was not expected to give and does not give accurate values for k_2/k_9 . In spite of the scatter, the data, nevertheless, indicate that k_2/k_9 does not vary considerably between 0 and 58°. This indicates that E_9 is approximately equal to E_2 . If we accept $E_2 = 0$ kcal.,⁶ our data thus substantiate the relatively low value of $E_9 = 1$ kcal. reported by Trotman-Dickenson and co-workers.⁴

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, THE FRANKLIN INSTITUTE LABORATORIES, PHILADELPHIA 3, PENNA.]

Effect of Gases on the Conductivity of Organic Solids. I. The Anthracene-Iodine Interaction¹

BY M. M. LABES AND O. N. RUDYJ

RECEIVED MARCH 7, 1963

Although gases are generally thought to affect the surface conductivity of organic crystals alone, evidence is presented that the bulk dark conductivity of anthracene is increased in a sensitive, specific and reversible manner upon exposure to iodine.

Introduction

In several investigations of the effect of gases on the dark and photoconductivity of organic crystals,² it has

(1) Supported by the U. S. Army Chemical Center under Subcontract SCE-17250-60 with Melpar, Inc.

(2) (a) A. T. Vartanyan, *Doklady Akad. Nauk S.S.S.R.*, **71**, 647 (1950); (b) A. G. Chynoweth, *J. Chem. Phys.*, **22**, 1029 (1954); (c) A. Bree and L. E. Lyons, *ibid.*, **25**, 384, 1284 (1956); (d) A. Bree and L. E. Lyons, *J. Chem. Soc.*, 5179 (1960); (e) W. G. Schneider and T. C. Waddington, *J. Chem. Phys.*, **25**, 358 (1956); (f) D. M. J. Compton and T. C. Waddington, *ibid.*, **25**, 1075 (1956); (g) T. C. Waddington and W. G. Schneider, *Can. J. Chem.*, **36**, 789 (1958).

generally been accepted that these phenomena are restricted to the surface. Thus in a sandwich cell provided with a guard ring, Waddington and Schneider^{2g} report no effect of oxygen on the photocurrent of anthracene, whereas in a surface cell a pronounced increase is observed.

These same types of surface effects on the conductivity have been observed for a large number of dye films exposed to gases.³ A particularly unusual example is the claim of the sensitivity of photoconduction in a

(3) A. Terenin, *Proc. Chem. Soc.*, 321 (1961).

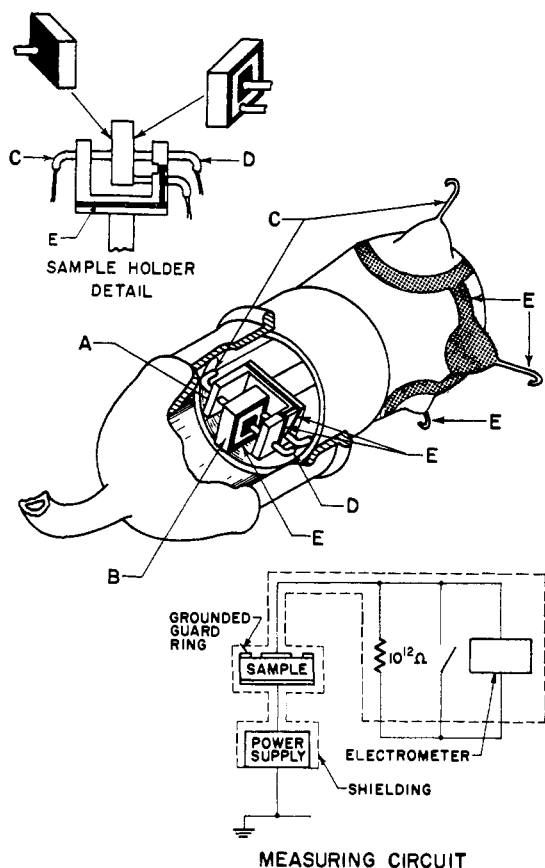


Fig. 1.—Measuring cell and circuit: A, sample holder; B, sample; C, high impedance current electrode; D, low impedance current electrode; E, guard ring.

fuchsin film to mercury vapor, a concentration of $\sim 10^{-3}$ mm. reportedly enhancing conduction by two orders of magnitude.⁴

Kearns, Tollin and Calvin⁵ have studied donor-acceptor interactions at a solid-solid interface; a typical experiment involves the deposition of a thin layer of *o*-chloranil on a film $\sim 5 \times 10^{-4}$ cm. thick of phthalocyanine covering an electrode system. They interpret their experiments as involving charge-carrier injection into the *bulk* of the phthalocyanine.

Proceeding from these ideas, it was our intention to examine cases of crystal-gas interactions in which the respective molecules could participate in complexing at the surface, but in which any observed effects would be reversed when the gas was pumped off. Should charge carrier injection occur into the bulk of such a crystal, it would depend on the nature and extent of the charge-transfer interaction at the surface. In a preliminary report on one such interaction involving anthracene and iodine, we pointed out the possibility of utilizing this effect in the electronic detection of chemical compounds.⁶ In this paper, we will discuss the anthracene-iodine system in detail, and in the following paper the reverse situation where the conductivity of an acceptor crystal, *p*-chloranil, is studied in the donor ambients ammonia and several aliphatic amines.⁷ The evidence available that a true bulk effect on the conductivity occurs will be presented.

(4) A. T. Vartanyan, *Doklady Akad. Nauk S.S.S.R.*, **94**, 829 (1954).

(5) G. Tollin, D. R. Kearns and M. Calvin, *J. Chem. Phys.*, **32**, 1013 (1960); D. R. Kearns, G. Tollin and M. Calvin, *ibid.*, **32**, 1020 (1960); D. R. Kearns and M. Calvin, *J. Am. Chem. Soc.*, **83**, 2110 (1961).

(6) M. M. Labes, O. N. Rudyj and P. L. Kronick, *ibid.*, **84**, 499 (1962).

(7) Preliminary report given at the Organic Crystal Symposium, October 10-12, 1962, Ottawa, Can.

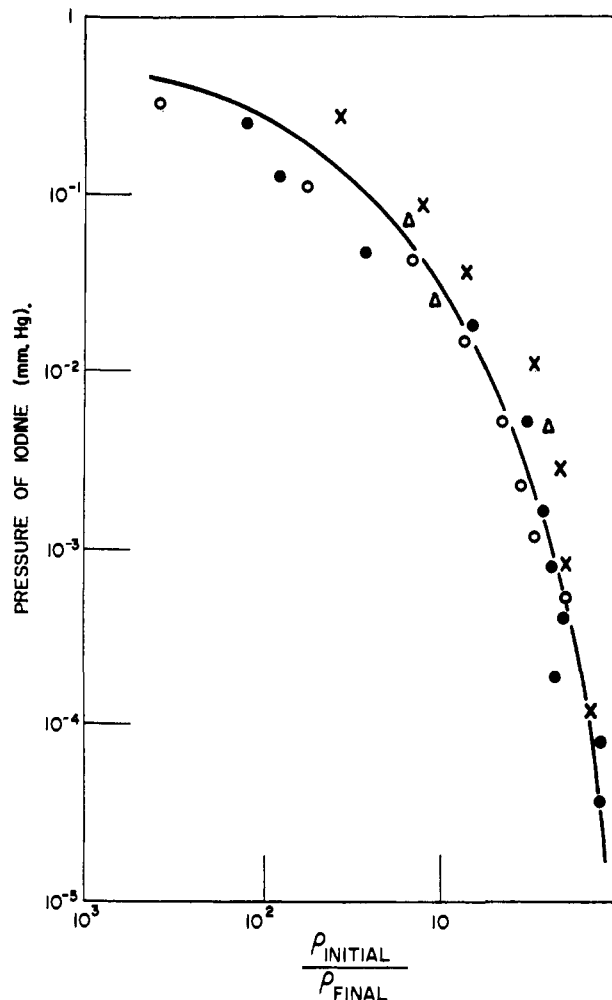


Fig. 2.—Log $\rho_{\text{init}}/\rho_{\text{final}}$ for four anthracene crystals (LAB plane) vs. log I_2 pressure.

Experimental

Anthracene single crystal slices were cut from large scintillation grade single crystals, obtained from the Harshaw Chemical Co., with large faces either parallel or perpendicular to the cleavage plane. A typical size crystal was $6.5 \times 6.5 \times 3$ mm. Electrodes in the configuration illustrated in Fig. 1 were painted onto the crystal using a conducting gold paint. The geometry was chosen to exclude surface conduction—a grounded guard ring around the low impedance electrode. The crystal was mounted in a Teflon holder fitted with gold-plated brass screws as electrode leads in the cell shown in Fig. 1. Potential surface current leakage paths on the Teflon holder and glass cell were eliminated by a suitable arrangement of grounded gold paint guard rings.

The bulk conductivity of the crystals was measured by observing the potential developed across an input resistor of the Cary Model 31-31V vibrating reed electrometer in series with the sample. A Keithley d.c. power supply model 240 was the voltage source. A block diagram of the circuit is given in Fig. 1. The cell shielding also effectively eliminates any illumination of the sample.

Most of the experiments were conducted in a static gas handling system in which the sample could be evacuated for several hours to a pressure of $\sim 10^{-6}$ mm. and then exposed to iodine vapor. The iodine vapor pressure was controlled simply by maintaining a trap containing iodine at different temperatures. In addition a flow system was employed in which the cell illustrated in Fig. 1 was modified by the addition of an outlet port, and an inert carrier gas swept through the cell. The carrier gas could be led through saturators containing iodine and/or other gases. Iodine concentrations in the gas phase were here determined by leading the carrier gas-iodine mixture through a potassium iodide solution adsorbate and titrating with standard thiosulfate solution.

Results

Figure 2 shows the reproducibility of the ratio of initial to final resistivity vs. iodine vapor pressure for 4

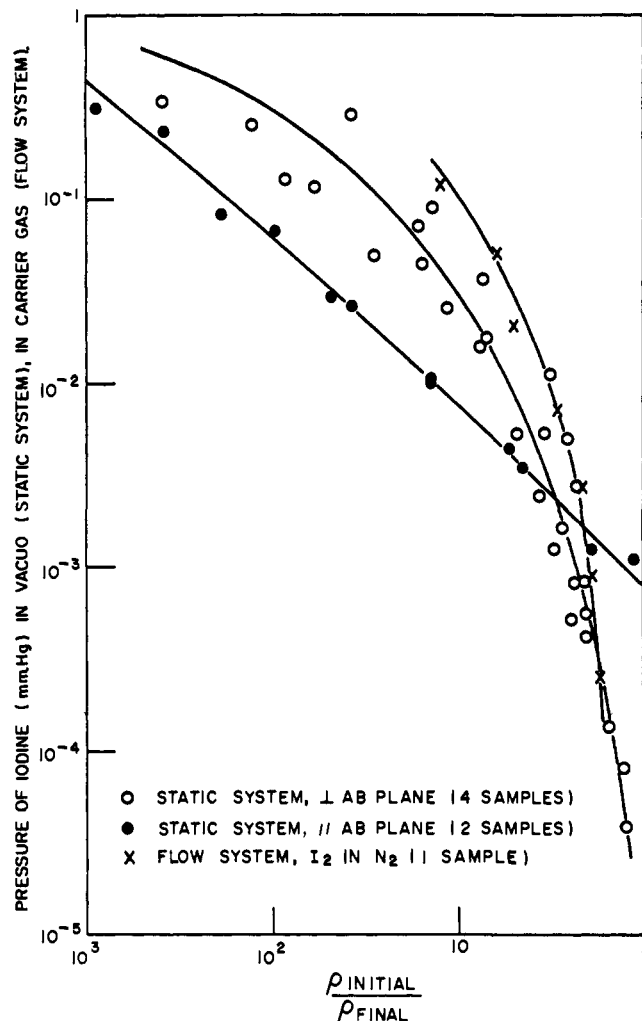


Fig. 3.—Log I_2 pressure (mm.) vs. log $\rho_{\text{initial}}/\rho_{\text{final}}$ for anthracene single crystals exposed to iodine vapor.

anthracene crystals, measurements being made perpendicular to the AB plane in the static system. Figure 3 gives a comparison of results both perpendicular and parallel to the AB plane in the static system and of results in the flow system. It can be seen that measurable changes in the conductivity occur at vapor pressures as low as 10^{-5} mm. in the static system, while in the flow system concentrations as low as 0.2 p.p.m. gave measurable changes. The change was found to depend on the iodine vapor pressure and the crystal orientation. Parallel to the AB plane the magnitude of the response is greater at a given iodine concentration, but the crystal is not as sensitive to low concentrations of iodine as it is perpendicular to the AB plane.

The change in conductivity occurs quite rapidly; in the flow system response began in less than 10 sec. after exposure. It reached 50% of its equilibrium value in 30 sec.; no further change was observed after 20–30 min. In the static system the maximum response occurred in less than 3 min. When the iodine flow over the crystal is stopped or the static system is pumped down to a hard vacuum, the resistivity returns to its original value. At the higher concentrations, however, a very long pumping time is required before the original resistivity is approached.

When an anthracene crystal is exposed to much higher concentrations of moist air (~60% humidity), sulfur dioxide, oxygen or hydrogen chloride, almost no change in the bulk dark conductivity is observed. Nitrogen dioxide, however, does affect the conductivity in a partially irreversible and quite non-reproducible

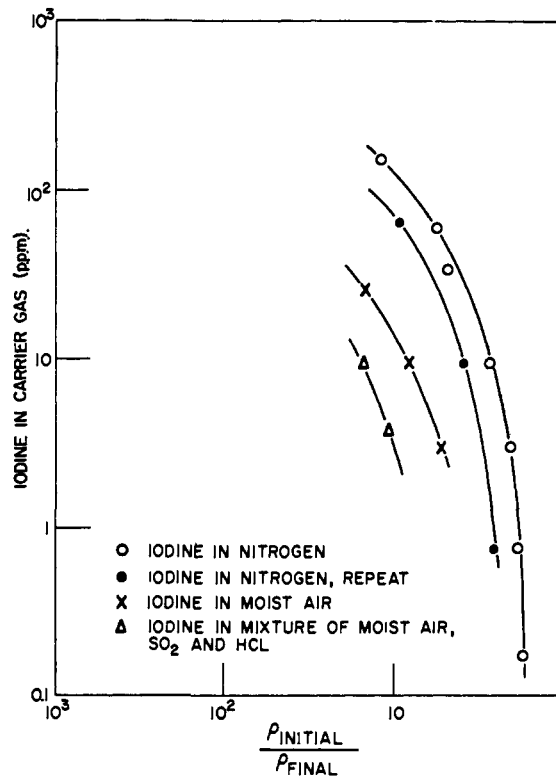


Fig. 4.—Log $\rho_{\text{initial}}/\rho_{\text{final}}$ vs. log $[I_2]$ in p.p.m. for flow system (flow rate 1 l./min.).

manner. These data, taken on several crystals, are given in Table I.

TABLE I
EFFECT OF VARIOUS GASES ON RESISTIVITY OF ANTHRACENE SINGLE CRYSTALS

Sample	Gas	Pressure, mm.	$R_{\text{initial}}/R_{\text{final}}$
I	Moist air (approx. 60% humidity)	22.5	1.0
	Sulfur dioxide	26.4	1.0
	Oxygen	22.0	1.2
	NO_2	0.01	28.1
II		.016	21.2
		.049	75.6
		.48	136.6
		1.66	78.0
		8.2	113.0

When a mixture of hydrogen chloride, sulfur dioxide and water-saturated air was passed over an anthracene crystal at a rate of 1 l./min., no effect was observed, but when iodine was added, a response somewhat larger than expected based upon the iodine concentration was observed as illustrated in Fig. 4.

In an attempt to measure the effect of iodine on the activation energy for conduction, we were able to make measurements over the very small temperature range of 10–12° as shown in Fig. 5. Within this limited range, no change in activation energy could be observed.

One might expect to detect an unpaired spin concentration associated with the anthracene-iodine complex. The perylene-iodine complex at room temperature has about 3% free radical character but the coronene-iodine 1:1 complex has none.⁸ We have not been successful in isolating the solid anthracene-iodine complex.

Small anthracene crystals were sealed in evacuated quartz tubes under an iodine pressure of 0.2 mm.

(8) R. Sehr, M. M. Labes, M. Bose, H. Ur and F. Wilhelm, "Proc. Conference on Conductivity in Organic Solids, Duke University, April, 1960," Interscience Publishers, Inc., New York, N. Y., 1961, p. 309.

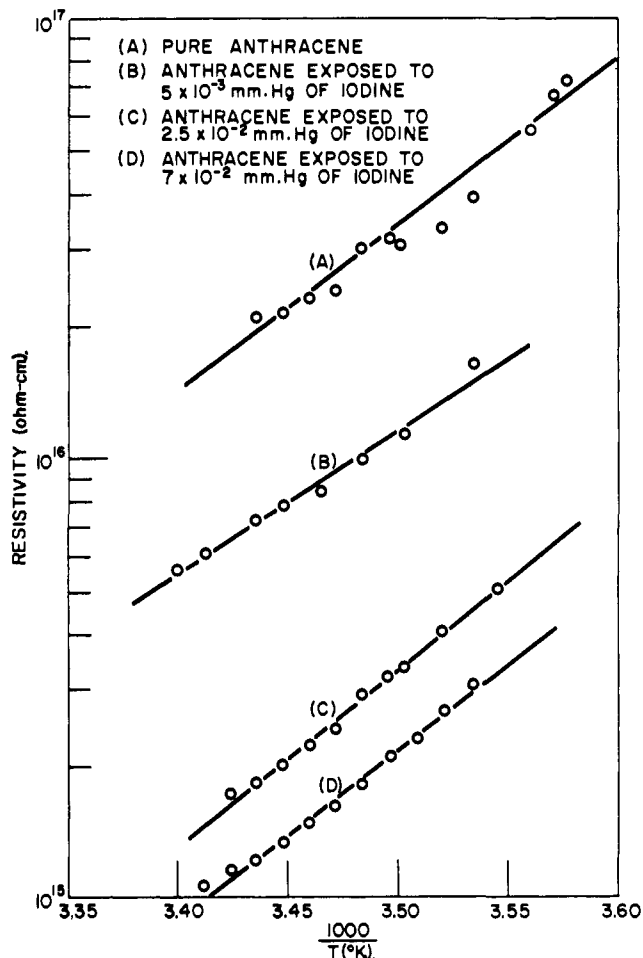


Fig. 5.—Determination of E_a of anthracene crystal in ambient containing iodine.

They were placed in the Varian V4531 multipurpose-cavity of the standard V4500 e.s.r. spectrometer operating in the X band using the V4560 100 kc. field modulation unit. No e.s.r. signal was observed.

However, if one assumes that a monolayer of complex is formed on the anthracene crystals and that this complex has a 1% free radical character, one calculates that 10^{12} molecules with free spins should be present. This is just at the lower limit of detection of the Varian instrument. Hence the experiment is inconclusive as to the presence or absence of complex at the surface.

Attempts to conduct the same type of experiment on other hydrocarbon crystals have been made with naphthalene and pyrene. We were unsuccessful because of the very high vapor pressure of naphthalene in studying its behavior, but pyrene responded in a manner similar to anthracene (Fig. 6).

Finally, when a Teflon plug of the same size as the anthracene crystals, or a stilbene crystal, was exposed to iodine no change in conductivity was observed.

Discussion

It would seem likely that the effects of gases on the conductivity of an insulating crystal should be restricted to a small surface layer, and hence guard ring circuitry would be expected to eliminate any perturbation of the current. Yet the experimental results described here suggest that a true bulk conductivity increase occurs. Several possible alternate explanations of such an increase must be considered.

One such explanation is that diffusion of iodine occurs easily into the bulk of the crystal. However, this seems unlikely since solid state diffusion is such a slow process. The only experiment on a molecular crystal

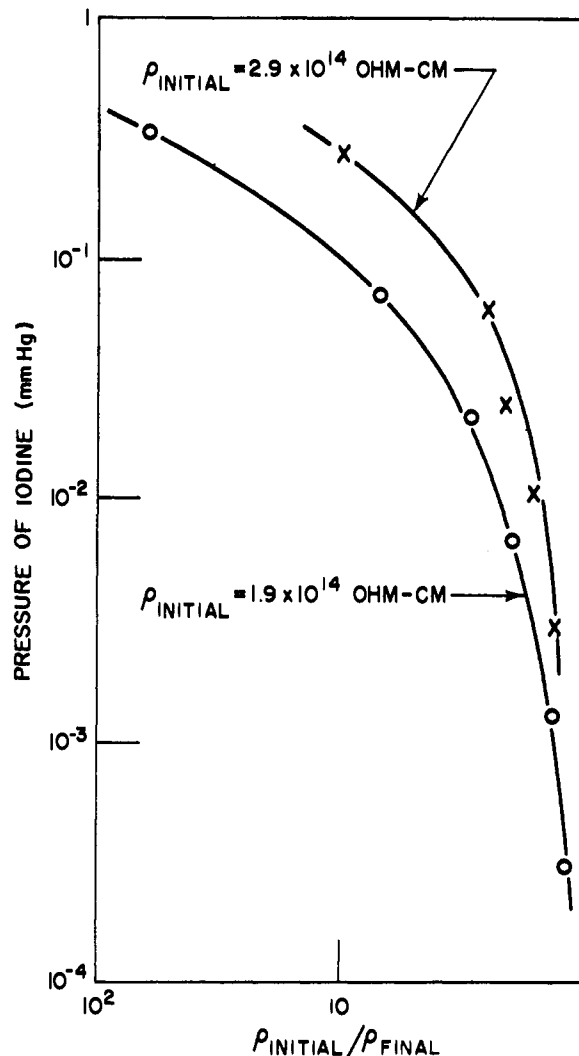


Fig. 6.—Log $\rho_{initial}/\rho_{final}$ for pyrene single crystals (\perp AB plane) vs. iodine pressure.

of pertinence is the measurement of the diffusion constant of anthracene-C-14 into anthracene which gave a value of $\sim 10^{-10}$ cm.² sec.⁻¹ at 450°K.⁹ Diffusion via cracks or voids might be expected to be more rapid, but hardly to yield the reproducibility from crystal to crystal observed in this work.

Another explanation of the effect observed is the possibility that the guard ring circuitry employed was ineffective. However, the experiments involving a Teflon plug substituted for anthracene suggest that no leakage path exists. The negative result with stilbene further implies that a material which might be expected to absorb iodine about as well as anthracene will not show a response due to a spurious surface current. Exposure to moist air, oxygen, etc., is known² to effect surface currents and the guard ring circuitry employed did eliminate the increased current in these cases.

Finally, it is possible that iodine by diffusing between the electrode and the crystal is changing the nature of the contact in such a manner as to cause an increase in dark current. Certainly, the effect of iodine is pronounced in the case of the liquid electrolyte electrodes employed by Kallmann and Pope¹⁰ and is also involved in the copper iodide electrode system.¹¹ We cannot at this date rigorously exclude this possibility but it seems

(9) J. N. Sherwood and S. J. Thompson, *Trans. Faraday Soc.*, **56**, 1443 (1960).

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

(11) H. Borofka, *Z. Physik*, **160**, 93 (1960); P. J. Reucroft, *J. Chem. Phys.*, **36**, 1114 (1962).

unlikely based on (a) the speed of the response of the crystal to iodine being faster than the expected rate of diffusion of iodine between the crystal-metal interface or (b) the passivity of the gold electrodes. However, iodine is a very reactive molecule and spurious effects may be difficult to avoid.

Thus, it seems most likely that a charge-transfer interaction at the surface of an organic crystal can cause carrier injection into the bulk. In the following paper, a further example of this phenomenon will be presented, and the nature of the interaction discussed more thoroughly.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, THE FRANKLIN INSTITUTE LABORATORIES, PHILADELPHIA 3, PENNA.]

Effect of Gases on the Conductivity of Organic Solids. II. The *p*-Chloranil-Amine Interaction¹

BY P. J. REUCROFT, O. N. RUDYJ AND M. M. LABES

RECEIVED MARCH 7, 1963

Ammonia and aliphatic amine vapors are shown to increase the bulk dark conductivity of *p*-chloranil single crystals. These data, when viewed in conjunction with previous results on the anthracene-iodine interaction, suggest that a rather general phenomenon exists—bulk conductivity of organic crystals being affected by donor-acceptor interaction at the surface.

Introduction

In the preceding paper,² an electron donor crystal, anthracene, was shown to undergo a sensitive, specific and reversible change in its bulk dark conductivity when exposed to iodine vapor, an electron acceptor. It was postulated that a donor-acceptor complex is formed at the surface of the anthracene, giving rise to carrier injection into the bulk of the solid, thus increasing its conductivity.

Data are herein presented dealing with the reverse situation where an electron acceptor crystal, *p*-chloranil, is exposed to the vapors of several amines. The effects on both the bulk and surface dark conductivity, current-voltage relationships, temperature effects and e.s.r. studies on these crystals are analyzed.

Experimental

Single crystals of *p*-chloranil were obtained by slowly evaporating benzene solutions of the compound. Typical crystals were hexagonal plates of thickness 0.5 to 1 mm. and 0.2 to 0.3 cm.² area. Prior to the crystal growing, the chloranil (Matheson, Coleman and Bell) was first recrystallized from benzene and sublimed under vacuum. Attempts to obtain single crystals from the melt were unsuccessful since chloranil slowly decomposes at temperatures slightly higher than the melting point. All other materials were used as supplied without further purification. Vapor phase chromatographic analyses indicated negligible amounts of impurities in the amine samples.

Resistance measurements at room temperature were carried out in a cell described previously,² while measurements at different temperatures were performed in the apparatus shown in Fig. 1. A convenient crystal sample holder employed in these studies is illustrated in Fig. 2. Temperature was varied from 10 to 70° by immersing the cell in an oil-bath which could be controlled to $\pm 0.2^\circ$, and the sample temperature was measured by means of a copper-constantan thermocouple attached directly to the sample holder. The pressure of ambient gas was measured directly by a mercury or oil manometer at pressures greater than 1 mm., and by means of a type PHG-09 Philips gage at pressures lower than this.

Conductive silver paint electrodes were arranged on the (001) planes of the solution-grown crystals, the current flow being measured perpendicular to this. Surface conduction was eliminated by arranging a grounded silver paint guard ring around the low impedance electrode (see Fig. 2). Possible surface leakage paths on the Teflon insulation were also eliminated by the suitable arrangement of grounded silver paint guard rings. In all resistivity measurements, which were performed with the instrumentation previously described,² the system was evacuated for several hours prior to exposure to amine or recording of an initial resistivity value.

Results

The effect of ambient vapor upon the bulk resistivity of chloranil crystals is expressed in terms of the ratio of the initial resistivity of the unexposed sample

(1) Supported by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, under contract No. AF 19(628)-1660. Preliminary report given at the Organic Crystal Symposium, Oct. 10-12, 1962, Ottawa, Can.

(2) M. M. Labes and O. N. Rudyj, *J. Am. Chem. Soc.*, **85**, 2055 (1963).

TABLE I
EXPOSURE OF CHLORANIL SINGLE CRYSTALS AT 22° TO AMBIENT GASES WITH ELECTRON DONOR AND ACCEPTOR PROPERTIES

Ambient gas	ρ_{init} , ohm-cm.	Pressure, mm.	$\rho_{\text{init}}/\rho_{\text{final}}$
Ammonia	3×10^{16}	20	1.7
Trimethylamine	1.5×10^{15}	20	12
Methylamine	4×10^{15}	20	24
Triethylamine	1.3×10^{16}	20	96
Diethyl chlorophosphate	3×10^{15}	0.46	0.32
Iodine	3×10^{15}	0.25	0.20

TABLE II
RELATION BETWEEN PRESSURE OF AMMONIA GAS AND TIME REQUIRED FOR MAXIMUM RESPONSE IN THE RESISTIVITY OF CHLORANIL AT 22°

Press. of ammonia, mm.	Max. response time, min.	Press. of ammonia, mm.	Max. response time, min.
0.4	7	3.36	2
0.72	4	8.86	0.5
1.7	3	22.2	.25
2.14	3	84.5	< .25

to the final resistivity attained after exposure, *i.e.*, $\rho_{\text{init}}/\rho_{\text{final}}$. This factor is shown in Table I for the exposure of chloranil to vapors with both electron donor and electron acceptor properties. Upon exposing chloranil to amine vapors a decrease in bulk resistivity is produced analogous to the effect of iodine upon anthracene,² but at much higher concentrations of amine. The effect with amines is in the order triethylamine > methylamine > trimethylamine > ammonia. In contrast to the effect of the amines, the exposure of chloranil to the vapor of iodine and diethylchlorophosphate produced an *increase* in the bulk resistivity. Since the initial resistivity is already very high (almost at the limit of measurement of our instruments, $\sim 10^{15}$ – 10^{16} ohm-cm.), this effect was not investigated further. Exposure of chloranil to hydrogen chloride or water vapor was found to produce a negligible effect upon the bulk resistivity.

In the amine-chloranil experiments the conductivity response reached a maximum value shortly after exposure and then decreased slowly to an equilibrium value slightly lower than the maximum value. The data in Table I refer to the equilibrium value. The time to reach the maximum value was found to depend upon the pressure of the gas, the maximum being reached faster at high pressures. Table II gives the time to reach maximum response as a function of gas pressure for a chloranil crystal exposed to ammonia.

Figure 3 shows equilibrium $\rho_{\text{init}}/\rho_{\text{final}}$ values plotted for chloranil exposed to various amines as a function of ambient pressure. This plot demonstrates clearly