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.

Effect of Gases on the Conductivity of Organic Solids. II. The *p*-Chloranil–Amine Interaction[1]

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

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 ±0.2°, 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.	ρ_{init}/ρ_{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.*, ρ_{init}/ρ_{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 ρ_{init}/ρ_{final} values plotted for chloranil exposed to various amines as a function of ambient pressure. This plot demonstrates clearly
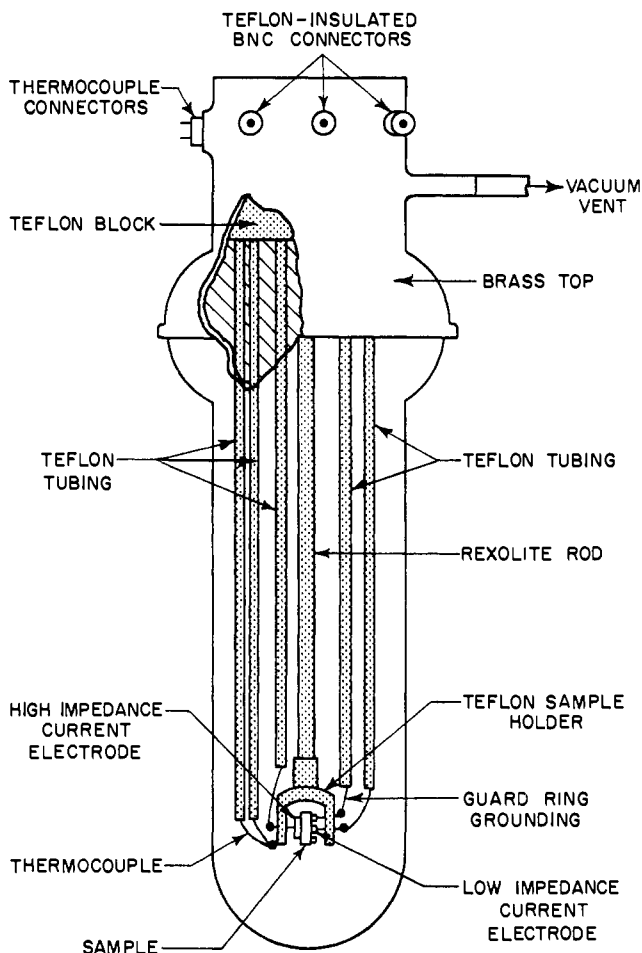
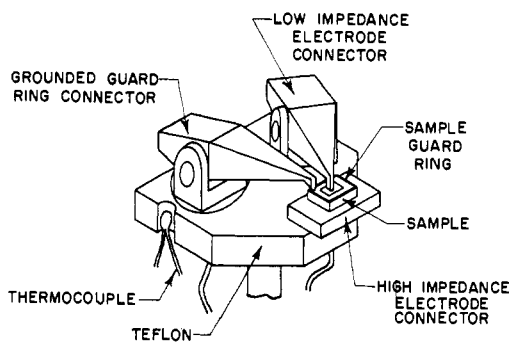Fig. 1.—High resistance cell used for measuring the bulk resistivity at different temperatures.

Fig. 2.—Brass–Teflon sample holder for crystals.

the increased effect on the bulk resistivity as one proceeds from ammonia to triethylamine.

In order to consider the experiments in terms of space charge limited current theory,[3-6] the form of the current–voltage relationship for a crystal of chloranil under vacuum and exposed to ammonia was examined. If the conduction current arises from the mobility of charge carriers thermally excited from some "valence" band to a "conduction" band, a current–voltage relationship of the form $I \alpha V$ is expected. However, if the conduction current arises from the mobility of excess carriers injected through the electrode or the crystal–gas interface, one might expect space charge limitation, in which case a current–voltage relationship of the form $I \alpha V^n$ where $n > 1$, is likely. Figure 4

(3) P. Mark and W. Helfrich, J. Appl. Phys., **33**, 205 (1962).

(4) A. Many, M. Simhony, S. L. Weisz and J. Levinson, J. Phys. Chem. Solids, **22**, 285 (1961).

(5) A. Rose, Phys. Rev., **97**, 1538 (1955).
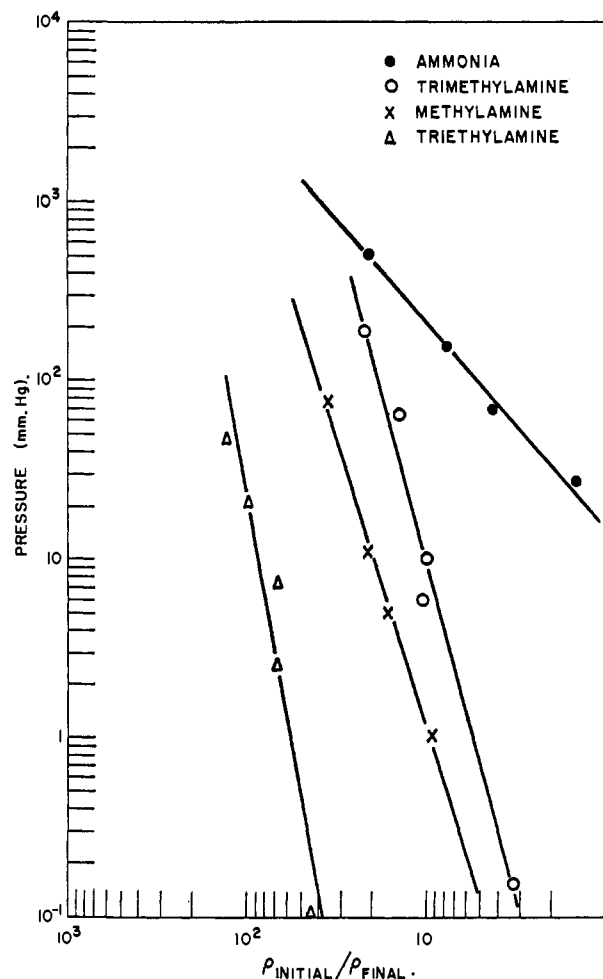
(6) M. A. Lampert, ibid., **103**, 1648 (1956).

Fig. 3.—Bulk resistivity change of chloranil single crystals on exposure to electron donor gases.

shows current density–field strength plots on a logarithmic scale for an unexposed chloranil crystal and the same crystal exposed to two pressures of ammonia. The current–voltage relationship is linear for the unexposed crystal up to about 4000 v./cm. and for the crystal in the presence of ammonia up to 6000 v./cm.; above these field strengths a V^2 law dependence was observed in both cases. Although departures from a linear current–voltage relationship can be observed, the relationship for a crystal exposed to an electron donor gas is very similar to that of the unexposed crystal, the only difference being the observation of a higher current level in the case of the exposed crystal.

The effect of ambient gas on the activation energy for conduction, E_a ($\rho = \rho_0 \exp E_a/kT$), is shown for a chloranil crystal exposed to ammonia in Fig. 5. Using the cell shown in Fig. 1 it was possible to measure the resistivity of the crystal over a temperature range from 10° to 70°. Figure 5 shows that in contrast to the anthracene–iodine system,[2] the activation energy of chloranil is quite sensitive to ambient pressure, decreasing with increasing ambient pressure. This effect was also found for chloranil exposed to triethylamine and methylamine as shown in Table III. In the case of trimethylamine, the same qualitative dependence of activation energy on ambient pressure was observed; however, the dependence of resistance on temperature became markedly irreversible at high pressures and temperatures, due to a reaction at the crystal surface between chloranil and amine.

At high pressures and temperatures a general tendency to react with the crystal surface was observed for all amines. However, at temperatures lower than 50°
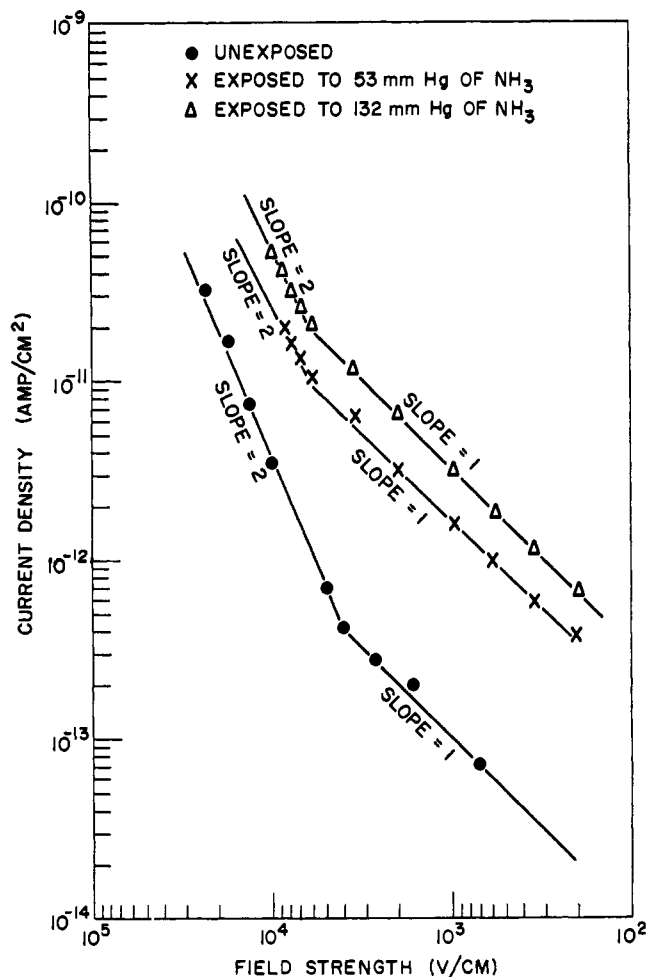
Fig. 4.—Current–voltage measurements for a chloranil single crystal.

and ambient pressures lower than 100 mm. the conductivity effect was found to be quite reversible and reproducible and no appreciable reaction was observed except in the case of trimethylamine. Since the reaction of chloranil with various amines is known to take place easily in solution[7–9] it appears likely that the postulated charge transfer complex at the surface is an intermediate in this reaction, the rate of reaction for the solid–gas being much less than for the same species in solution.

TABLE III

EFFECT OF AMBIENT GAS ON THE ACTIVATION ENERGY OF CHLORANIL

Ambient gas	Press., mm.	Activation energy, e.v.	Ambient gas	Press., mm.	Activation energy, e.v.
Methylamine	0	0.63	Triethylamine	0	0.85
	2	.51		2	.55
	13	.41		14	.44
	41	.29		43	.44

Considerable precautions were taken throughout to ensure that the bulk resistivity was being measured and any surface conduction between the measuring electrodes was eliminated by means of a grounded guard ring. In order to compare the effect of ambient gas on surface conduction and bulk conduction, measurements were made without a guard ring, with a guard ring painted on the crystal but not grounded, and

(7) D. Buckley, S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4880 (1957).
(8) H. B. Henbest, private communication.
(9) L. F. Fieser and E. L. Martin, *J. Am. Chem. Soc.*, **57**, 1844 (1935).
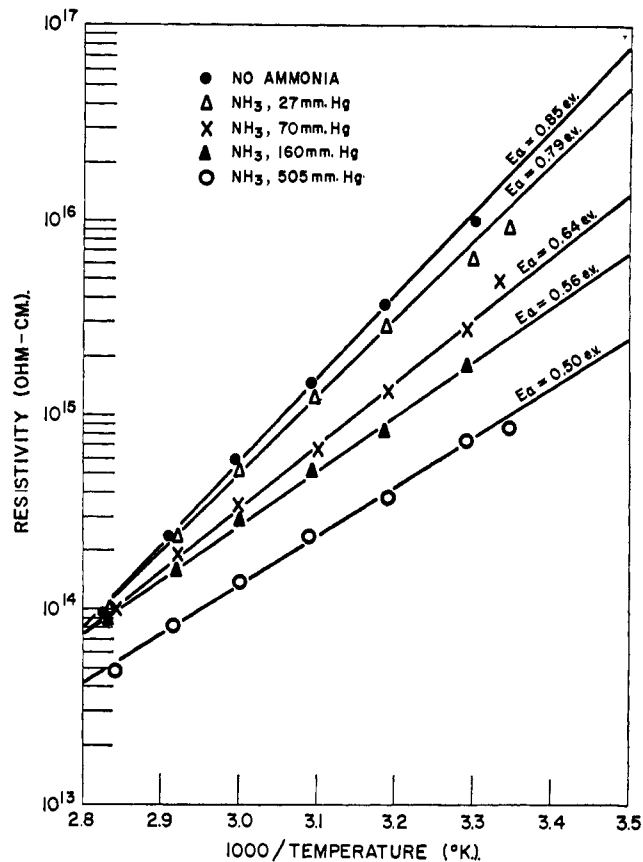
Fig. 5.—Determination of E_a for a chloranil single crystal exposed to various pressures of gaseous ammonia.

with a grounded guard ring. This comparison is shown graphically in Fig. 6 for trimethylamine and in Table IV for ammonia and methylamine. In these comparisons, the ratio of the initial resistance to the final resistance for the crystal without grounded guard ring is compared to the ratio of the initial resistance to the final resistance for the crystal with grounded guard ring. In the case of surface conductance it is meaningless to refer to resistivity, and the ratio is here considered as a ratio of resistance, *i.e.*, R_i/R_f.

TABLE IV

EFFECT OF AMBIENT GAS ON THE SURFACE AND BULK RESISTANCE OF CHLORANIL

Compound	Vapor press., mm.	Surface resistance — No guard ring, R_i/R_f	Guard ring not grounded, R_i/R_f	Bulk resistance guard ring grounded, R_i/R_f
Ammonia	1	. . .	16	1
	2	. . .	24.4	1.55
	3	. . .	31	2
	5	. . .	40	2.75
	8	. . .	40	3.7
	15	. . .	40	4.4
	30	. . .	40	4.4
Methylamine	0.25	38	76	37
	0.5	66	106	46
	1.0	112	111	59
	2.0	192	120	70
	5.0	270	131	76
	10.0	270	140	76

The conductivity response is five to ten times greater without a grounded guard ring in all these cases. It seems likely that the reduction in conductivity response on going from a crystal without grounded guard ring to a crystal with a grounded guard ring is due to the elimination of surface conduction. The
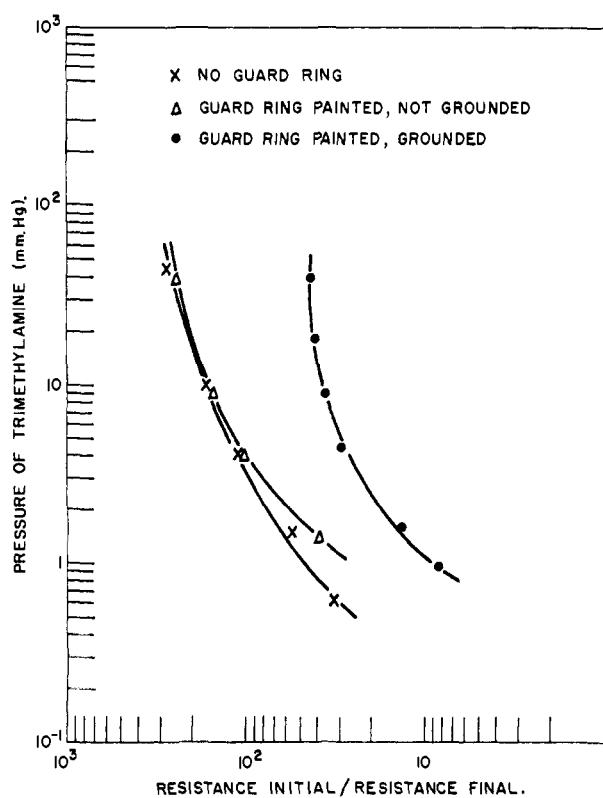
Fig. 6.—Effect of trimethylamine on the bulk and surface resistance of a chloranil single crystal.

on surface area, is supporting evidence for the hypothesis that a surface charge-transfer process is taking place.

Discussion

The observation of the increase in bulk conductivity of either donor or acceptor crystals when exposed to acceptor or donor vapors, respectively, appears to be a rather general phenomenon. In the anthracene–iodine experiments,[2] one of the unfortunate features is the great reactivity of iodine making spurious effects difficult to avoid. There was reason to believe that *any* organic material exposed to iodine would undergo a marked increase in its conductivity. The observation of a *decrease* in conductivity of chloranil when exposed to iodine vapor lends support to the important role of surface charge-transfer complexing to the carrier injection process. In the amine–chloranil systems there is a rough parallelism between the ionization potential of the donor vapor and its effectiveness in increasing the conductivity. Thus, the phenomenon is pictured as: donor–acceptor charge-transfer occurs between the crystal and an adsorbed layer. Under the influence of the applied field, charge separation can then occur. With a donor vapor, this can be viewed as electron injection, whereas in the anthracene–iodine case hole injection occurs.

The departure from a linear current–voltage relationship appears to occur at a slightly higher voltage for a chloranil crystal in the presence of ambient ammonia compared to the unexposed crystal. While this difference is small, it suggests that the gas is in some way increasing the number of volume generated carriers by a process independent of the electrode injected space-charge-limited current process. If the latter process were being aided, one would expect a departure from linearity at lower voltages for the exposed crystal. On the contrary, the effect of ambient gas seems to be analogous to the effect that illumination produces in certain crystals.[11]

Some differences were observed between the amine–quinone systems and the anthracene–iodine system. In this latter system, no change in E_a was observed upon exposing to ambient iodine, although a large change in conductivity was observed and no unpaired spin concentration was observed for an anthracene crystal or powder in contact with iodine. It should be pointed out, however, that the temperature was only varied by 10–12° in the E_a determination for anthracene, so that small changes could easily have been obscured. Since the relationship between e.s.r. phenomena and the charge-transfer interaction is poorly understood, it is hard to draw any conclusions from the absence of an e.s.r. signal in the anthracene case. The coronene–iodine complex has indeed been reported to give no e.s.r. signal,[10] although it is definitely a charge transfer complex, and the solid anthracene–iodine complex has not been isolated.

An explanation of why such a surface interaction is not restricted to affecting the surface conductivity alone and a plausible model for the injection of carriers is not discernable at this point. One possibility which is being explored is that ambient gas exerts its effect at the crystal–electrode interface exclusively. Experiments masking surfaces and/or electrodes and varying electrode geometry are in progress and will be reported at a later date.

Acknowledgment.—The coöperation of C. J. Lin in performing the e.s.r. measurements is gratefully acknowledged.

residual effect on the bulk resistivity can only be found in the cases where a donor–acceptor interaction can occur.

If this donor–acceptor interaction occurs at the surface one might expect to detect an e.s.r. signal. To test this, two samples of chloranil in a sealed quartz tube under 1 atm. of ammonia were examined in a standard V4500 Varian e.s.r. spectrometer, the samples being placed in a V4531 multipurpose cavity. The spectrometer was operated in the X band using the V4560 100-kc. field modulation unit. One sample of chloranil was a single crystal weighing approximately 0.1 g. and having a surface area of 1 cm.[2]. In this case no signal was found. The second sample consisted of 0.1 g. of chloranil ground to a fine powder and here a signal was obtained. A similar powdered sample in contact with air gave no signal, demonstrating that the unpaired spins could not have been produced by the grinding process. The signal was estimated at 10^{14}–10^{15} unpaired spins for this sample and was without structure, having a g-value of 2.0043 and a line width, between points of maximum slope, of 11 gauss. While unpaired spins may be produced in the single crystal specimen, they are too few in number to be observed. From the absence of this signal and the single crystal surface area, it was estimated that less than 1% of the adsorbed molecules (assuming a monolayer) are giving rise to an unpaired spin. This conclusion depends, of course, upon the validity of assuming that a monolayer of adsorbed molecules is formed at pressures of 1 atm. In the absence of exact isotherm data this conclusion must necessarily be tentative, but appears reasonable in view of reports that many charge transfer complex crystals are found to have from 1–3% free radical character.[10] Nevertheless the presence of unpaired spins in the powdered chloranil–ammonia system, and the added fact that the signal seems to depend strongly

(10) R. Sehr, M. M. Labes, M. Bose, U. Ur and F. Wilhelm, "Symposium on Electrical Conductivity in Organic Solids," Interscience Publishers, Inc., New York, N. Y., 1961, p. 309.

(11) For example, see G. H. Heilmeier and G. Warfield, *J. Chem. Phys.*, **38**, 163 (1963).