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Electric Conductivity and Paramagnetic Resonance of Charge-Transfer Complexes of Chloranil with Trimethylamine and Triethylamine

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Abstract—The conditions for the formation of charge-transfer complexes of *p*-chloranil with aliphatic amines were examined. The formation of the stable CT complex was found only in the reaction of gaseous trimethylamine and triethylamine with solid choranil. Electric conductivity of the complexes in form of pressed pellets and of thin films was measured as a function of temperature and pressure of amine vapour. The doping effects of ambient amine, viz. an increase in conductivity and a decrease in activation energy were observed. The effects were due to an increase in the ionic character of the complex, revealed as a rise of the ESR-absorption and a modification of the IR spectrum.

The electric and magnetic properties of charge-transfer (CT) complexes of *p*-chloranil (ChA) with aromatic amines, e.g., with *p*-phenylenediamine (PDA), have been widely investigated.(1,2) There is, however, only scarce information available on CT-complexes of chloranil with aliphatic amines. The absorption spectra of aqueous, ethanolic, and CCl_4-solutions of chloranil and several aliphatic amines have been reported.(3–6) The effect of gaseous ammonia and amines on the conductivity of single crystals(7–9) and of thin layers(10) of chloranil has also been studied. In all these papers, the formation of CT-complexes has been tacitly assumed, and the nature of the reaction products has not been scrutinised. There is, however, some evidence for the formation of chloraminequinones in the reaction of chloranil with aliphatic amines in benzene- or amine-solutions.(11,12)

Having realized the complexity of the chloranil–amine interaction, we studied more thoroughly the reaction of solid *p*-chloranil with gaseous aliphatic amines, viz., trimethylamine (TMA), triethylamine (TEA), diethylamine, di-*n*-propylamine, diisopropylamine, di-*n*-butylamine, isopropylamine, *n*-butylamine, isobutylamine, sec-butylamine, tert-butylamine, cyclohexylamine, and ammonia.

In the first section of this paper a description is given of the preparation and identification of products of the reaction of *p*-chloranil with these amines. Then we report the electric conductivity and ESR of two CT-complexes: ChA . TMA and ChA . TEA, as well as of ChA . PDA complex studied for comparison. In the third section of the paper the doping effects of ambient amine on the conductivity, ESR- and IR-spectra of the ChA . TMA complex are described.

1. Preparation and Identification

Materials. *p*-Chloranil (Schuchardt) was twice sublimed in vacuum. PDA (FOCh) was twice sublimed in vacuum and then zone-melted. Colourless crystals obtained after ca. 100 zone-passes were surprisingly stable and did not oxidize in air for several months. Amines (Fluka, FOCh) were purified by destillation and, if necessary, by column chromatography and checked on purity by the gas-chromatography. TMA and TEA were additionally dried over $MgSO_4$.

Powdered chloranil was exposed to amine vapours in a simple vacuum apparatus consisting of a reservoir of liquid amine, a buffer bulb and a reaction chamber. The reaction was being carried out at the room temperature and lasted for several weeks or even several months. In the course of the reaction the material was ground several times and eventually degassed at 80 °C and ca. 0.1 Torr for a few hours. In some experiments solid chloranil was dissolved in liquid amine (TEA, di-*iso*-propylamine, butylamines) or in solution of amine in an appropriate solvent (benzene, cyclohexane, methylene chloride). The products of the reaction of chloranil with gaseous amines were analyzed without a further purification. The elemental analysis (C, H, N, Cl) and conductometric determination of Cl^- ion in aqueous suspensions of the products were carried out. The following conclusions may be drawn from the obtained results:

reaction mechanism (consecutive reaction with the fast, bimolecular first step followed by slow, monomolecular rearrangement).

The charge-transfer ChA . PDA complex was prepared by a thorough grinding of the components in stoichiometric amounts, pressing them in pellets and grinding again. The procedure was repeated several times and the ground material was eventually heated in vacuum to remove unreacted components. The IR spectrum of the material did not differ from that of the complex precipitated from solution(13) but by the presence of faint peaks of free PDA.

2. Electric Conductivity

Electric conductivity of the three CT-complexes (ChA . PDA, ChA . TMA, ChA . TEA) was studied on materials in form of pressed pellets and of thin films.

The pellets 2–5 mm thick and 10 mm in diameter were moulded from the materials prepared as described above. The electrodes and a guard ring made of gold leaf 1 μm thick were pressed onto the faces of the pellets in course of the moulding. The arrangement of electrodes is shown in Fig. 2. The pellet was mounted between platinum contacting electrodes in an aluminium block provided with two heaters and a copper–constantan thermocouple. Hot junction of the thermocouple was touching the guard ring. A constant voltage from a dry-cell battery was applied to one electrode, the second being connected to an electrometer. Long-lasting polarization effects were observed after each change of voltage, the steady current, however, was ohmic for voltages ranging from 2 to 240 V. The measurements were taken in vacuum (10^{-3} Torr) both in heating and cooling runs, after the thermal equilibrium of the heating block with the sample was attained.

Thin layers of the complexes were prepared immediately within the chamber in which their conductivity was measured (Fig. 1).

An aluminium block (2) provided with a quartz plate with gold electrodes (5) painted on it was hung up on a bare end of a Dewar flask (1) inside a vacuum vessel (not shown in the figure). Heat contacts between the quartz plate, aluminium block and Dewar flask were ensured owing to silicone grease. The Dewar flask was filled with a suitable coolant and a thin layer of chloranil (approx. 10 μm thick) was deposited by sublimation onto the quartz plate at -70 °C. Then the layer was heated up to the room temperature and amine vapour was introduced. The reaction started immediately resulting in dramatic changes in electric resistance of the layer (by as much as 7 orders of magnitude). The constancy of resistance

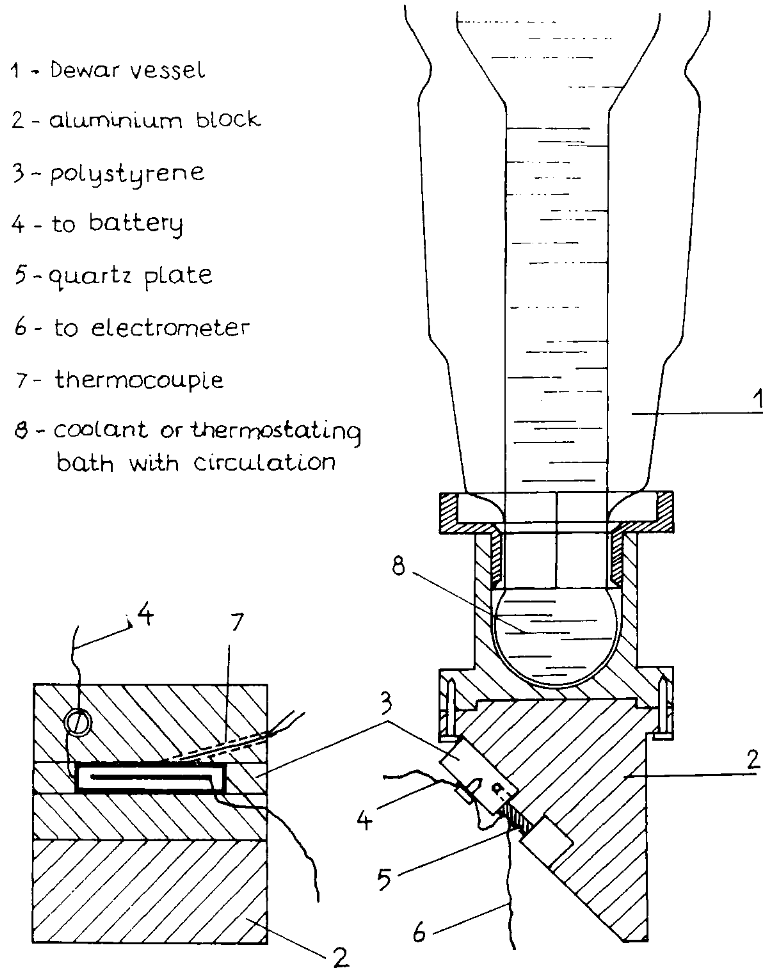

Figure 1. Sample-holder for preparation and measurement of electric conductivity of the thin layers of the complexes.

(attained after some dozens of hours) argued for the completion of the reaction. The amine vapour was pumped off and the layer degassed at 10^{-3} Torr and 60 °C approx.

In a similar way thin layers of the ChA . PDA complex were prepared except that amine was sublimed onto the layer of chloranil (reverse sequence of deposition, deposition in turns, and simultaneous sublimation of the components were applied as well).

The electric resistance of a pellet and of a thin layer of the ChA . PDA complex is shown in Fig. 2.

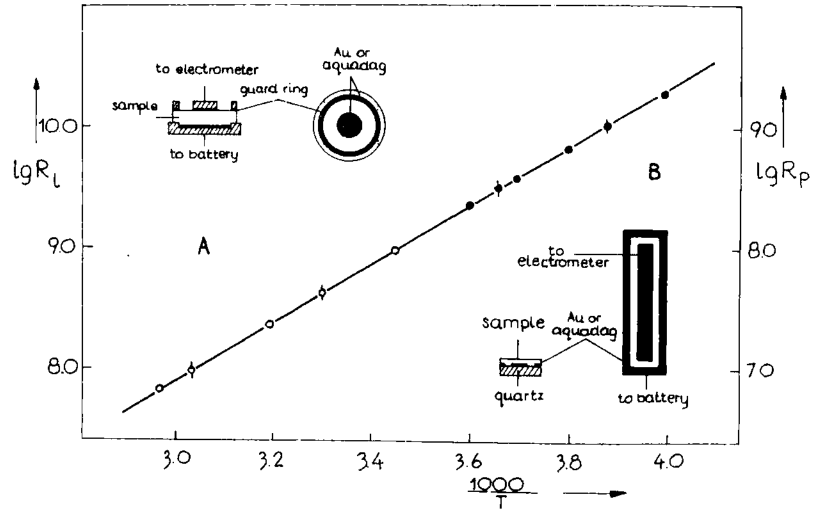

Figure 2. Electric resistance of a pellet (open circles, right-hand scale) and a thin layer (dots, left-hand scale) of the *p*-chloranil-*p*-phenylenediamine complex. ●, ○—heating runs, ⏀, ⦶—cooling runs.

The geometrical factor for the conversion of the resistance of the layer into resistivity being unknown, we shifted one ordinate axis to bring the graphs for the layer and for the pellet to coincide, a procedure allowed by the equality of activation energies in both types of the samples. The thickness of the layer as well as the method of preparation had no effect on the value of the activation energy and only a slight one on the value of the resistance.

Similar results were found for the ChA . TMA complex (Fig. 3).

The resistance of the ChA . TEA complex decreased sharply with

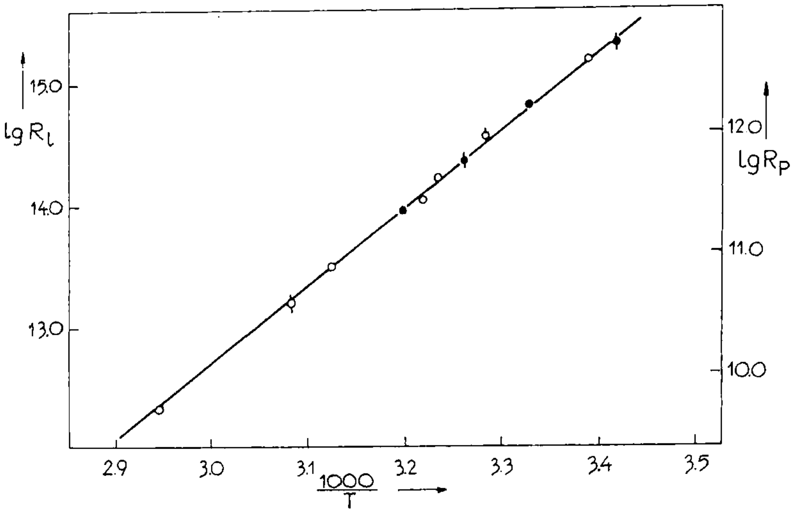

Figure 3. Electric resistance of a pellet (open circles, right-hand scale) and a thin layer (dots, left-hand scale) of the *p*-chloranil–trimethylamine complex. ●, ○—heating runs, $\underset{|}{\overset{|}{\bullet}}$, $\underset{|}{\overset{|}{\circ}}$—cooling runs.

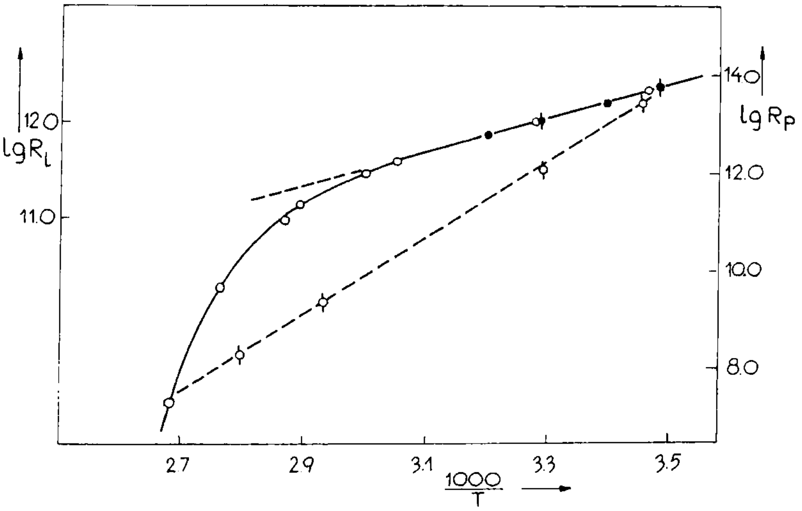

Figure 4. Electric resistance of a pellet (open circles, right-hand scale) and a thin layer (dots, left-hand scale) of the *p*-chloranil–triethylamine complex. ●, ○—heating runs, $\underset{|}{\overset{|}{\bullet}}$, $\underset{|}{\overset{|}{\circ}}$—cooling runs.

TABLE 1 Electric Properties of the Chloranil-amine Complexes

Complex	ϵ† (eV)	ρ_{20} (ohm.cm)	Reference
ChA.PDA	0.46	10^{10}	This work
ChA.PDA	0.43	10^{9}	14
ChA.PDA	0.46	1.5×10^{9}	15
ChA.PDA	0.58	5×10^{10}	16
ChA.TMA	1.20	$10^{14} - 10^{15}$	This work
ChA.TEA‡	0.71	$10^{15} - 10^{16}$	This work

† Evaluated according to the relationship $\rho = A \exp(\epsilon/kT)$.
‡ Below 60 °C.

temperature above 60 °C approx. (see Fig. 4), the effect being perhaps due to the onset of plasticity rather than to any chemical changes of the sample. (In the second run taken after the cooling of the pellet to the room temperature the same behaviour was observed.)

The values of the activation energies and the resistivities of the complexes are shown in Table 1 together with literature data for the ChA . PDA.

A satisfactory agreement of our values with literature data for the ChA . PDA complex argues for the correctness of our methods of preparation.

3. Doping Effects

The ChA . TMA complex when exposed to TMA vapour absorbs considerable amounts of amine under swelling. The absorption is accompanied by marked changes in electrical resistance, in IR spectrum, and to a minor extent in ESR absorption.

Thin layers of the complex prepared as described above were exposed to TMA vapour, and the temperature dependence of the electric resistance at an appropriate TMA pressure (ranging from 10 to 700 Torr) was investigated. The results are shown in Fig. 5.

The resistance of the layer at the room temperature decreases by 3 orders of magnitude at 700 Torr of ambient amine but the effect diminishes at higher temperatures. The doping effect is entirely reversible and in vacuum the initial value of resistance is restored.

An ESR absorption signal was observed in transient system in the X-band using a non-commercial spectrometer with the detection

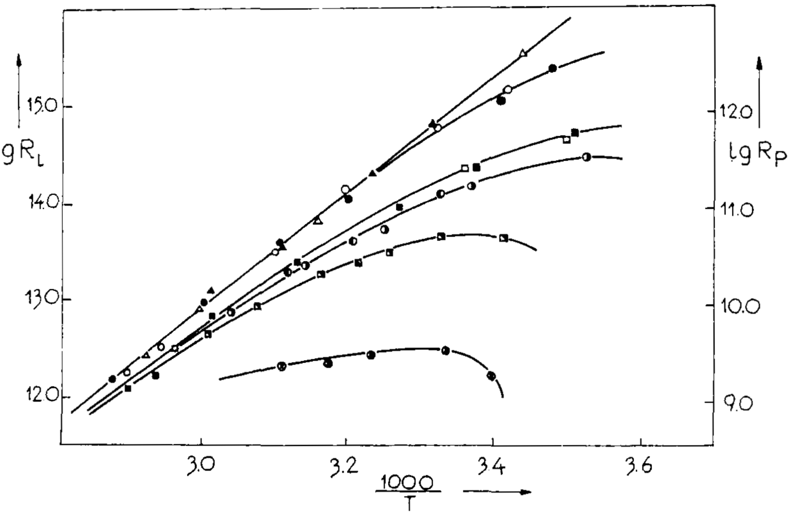

Figure 5. The effect of ambient amine on the electric resistance of a thin layer of the *p*-chloranil–trimethylamine complex (left-hand scale). ●—first run, (T ↑), $p = 10^{-1}$ Torr; ■—(T ↑), □—(T ↓), 40 Torr; ◑—(T ↑), ◐—(T ↓), 100 Torr; ◩—(T ↑), ◪—(T ↓), 270 Torr; ⊗—(T ↑), 675 Torr; ○—last run, (T ↓), 10^{-1} Torr. ▲—(T ↑), △—(T ↓)—electric resistance of a pellet at 10^{-3} Torr (right-hand scale).

level of 10^{14} unpaired spins in a sample. The ChA . TMA complex prepared as described above and thoroughly degassed showed a faint signal approximately 5 Gs wide, corresponding to the concentration of unpaired spins $N = 5 \times 10^{17}$ g^{-1}. This material was then brought in contact with TMA vapour at an appropriate pressure (10–700 Torr) for several dozens of hours. Then it was weighed in a capillary tube, additionally saturated with amine at the same pressure as previously and eventually sealed at the given TMA pressure. The doping effect manifested itself by an increase in ESR absorption without a broadening of the signal. The results are shown in Fig. 6. The room-temperature values of the resistance of a thin layer of the complex at various pressures of TMA are also given in the figure.

The IR spectra of *p*-chloranil (A), of the ChA . TMA complex obtained in a 9-months' synthesis and degassed at 80 °C for 3 hours (B), and of TMA . HCl (C), all taken in KBr wafers, are shown in Fig. 7.

The spectrum of the complex displays the main features of the

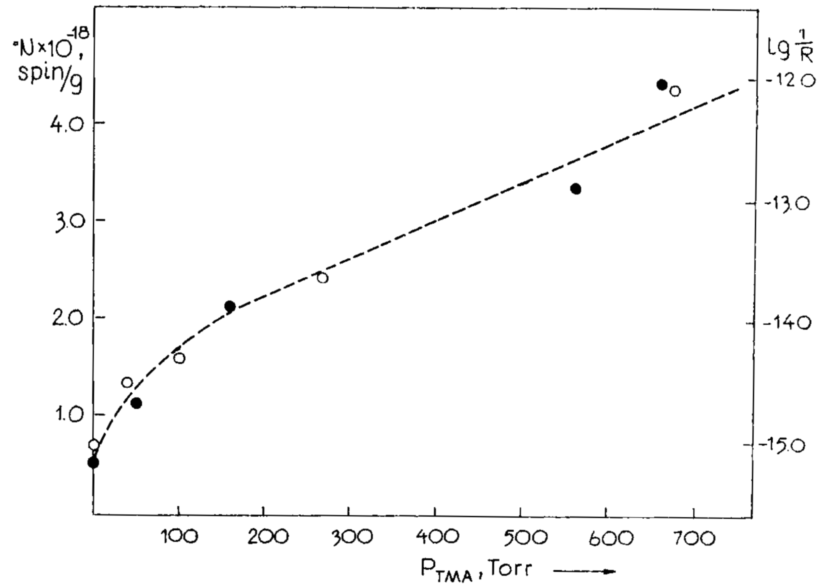

Figure 6. Spin concentration (dots, left-hand scale) and the electric conductivity of a thin layer of the complex of *p*-chloranil with trimethylamine (open circles, right-hand scale) at various pressures of ambient amine.

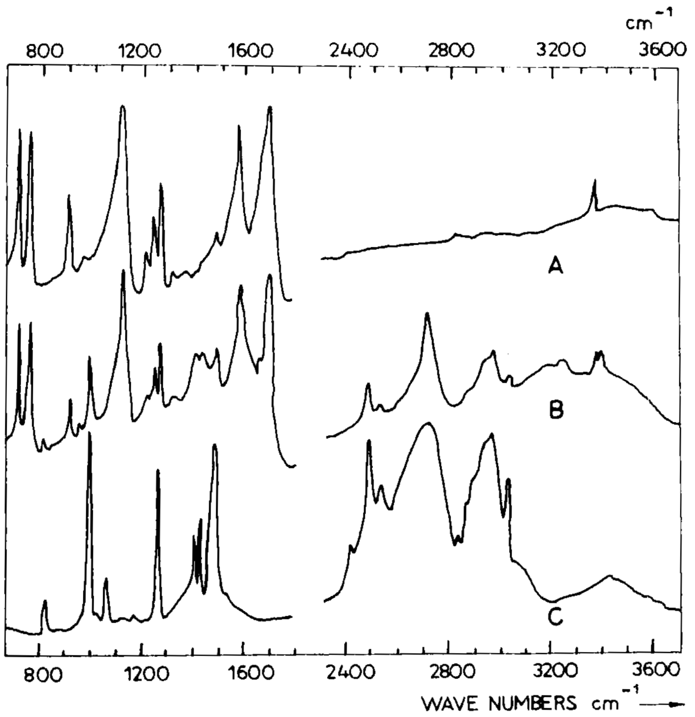

Figure 7. IR spectrum of *p*-chloranil (A), *p*-chloranil–trimethylamine complex (B), and trimethylamine hydrochloride (C) taken in KBr wafer.

spectra of chloranil and, oddly enough, of TMA$^+$-cation. The band system of the chloranil spectrum does not change substantially upon complexing except by the decrease in the 910 cm^{-1} band and the splitting of the carbonyl band near 1680 cm^{-1}. In the last respect the spectrum resembles that of the *p*-chloranil-dimethylaniline complex.(17)

In Fig. 8 the relevant regions of the spectrum of the complex saturated with TMA at ca. 700 Torr (A) are shown together with the spectrum of the degassed material (B), i.e., with the spectrum (B) of Fig. 7.

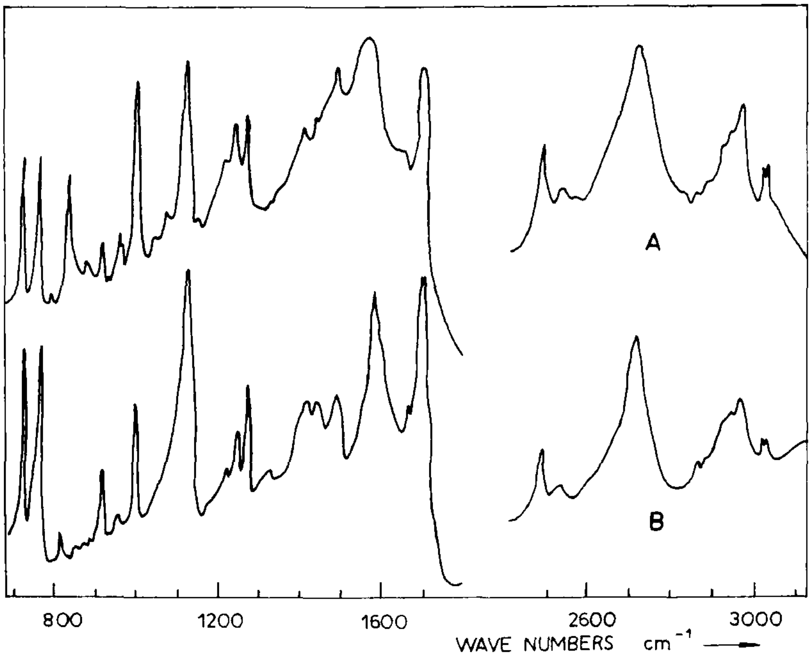

Figure 8. The effect of ambient amine on the IR spectrum of the *p*-chloranil-trimethylamine complex. IR spectrum of the complex saturated with amine at 700 Torr (A). IR spectrum of degassed sample (B).

The main features of the spectral changes caused by excess amine are:

i. an increase in TMA$^+$ bands at 990 and 825 cm^{-1} as well as a general increase in broad absorption beyond 2500 cm^{-1},

ii. building up of the absorption near 1550 cm^{-1} accompanied by the diminution of the carbonyl 1680 cm^{-1} band.

The effects are compatible with the increase in ionic character of the complex under the formation of choranil anion-radical characterized by strong bands at 1524 and 1540 cm^{-1}.(18)

All the changes in the IR spectrum due to saturation with amine are reversible and vanish after the degassing of the sample.

The following conclusions can be drawn from the experiments:

i. Chloranil forms with trimethylamine a relatively weak complex in terms of Kainer's classification(17) with substantially neutral ground state.

ii. The bonding type changes to the dative one in a non-stoichiometric complex containing excess amine. The effect increases with an increasing amount of amine and is reversible when amine is removed.

iii. Relatively small changes in ESR absorption when compared with distinct modification of the IR spectrum and the increase in electric conductivity suggest an extensive spin-pairing in the radical state of the complex.

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