

MOLECULAR COMPLEXES OF 1,4-DIAZABICYCLO[2,2,2]OCTANE WITH CHLORANIL AND BROMANIL

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Molecular complexes of 1,4-diazabicyclo[2,2,2]octane (DABCO) with chloranil and bromanil have been prepared in solution. Measurement of the respective absorption and EPR spectra indicated that complexes with complete charge transfer were formed in the studied systems. Electric conductivity measurements have been carried out with solid poly-crystalline compressed samples. Temperature dependence of the conductivity indicates that the both complexes show semiconductor properties with activation energies 0.56 and 0.60 eV for DABCO-chloranil and DABCO-bromanil complexes, respectively.

Molecule of 1,4-diazabicyclo[2,2,2]octane (DABCO), having two basic nitrogen atoms and cage structure, is a suitable nucleophilic reagent with catalytic activity¹. Low value of ionization potential (6.5 eV) of this molecule² makes it a strong electron-donor of *n* type. *E.g.* with tetracyanoethylene (electron affinity 1.6 eV (ref.³)) DABCO interacts to give a molecular complex with complete charge transfer⁴. Molecular complexes with a partial charge transfer are formed with weak acceptors as *e.g.* I₂ (ref.⁵) and Br₂ (ref.⁶).

The present paper deals with formation and physico-chemical properties of DABCO complexes with chloranil and bromanil in various solvents and in solid phase.

EXPERIMENTAL

All the chemicals used were commercial products (Lachema) and were purified by usual laboratory procedures. The molecular complexes were prepared by mixing of solutions of DABCO with the corresponding quinone in the presence of air at the laboratory temperature. The absorption spectra were measured with a Specord UV VIS apparatus (Zeiss, Jena). EPR spectra were measured with Spectrometer ER-9 (Zeiss, Jena).

The polycrystalline complexes were prepared by crystallization from benzene. After drying they were tableted at the pressure of 6500 kp/cm² using a DP-36 press E. Hammerschmidt. The tablets were coated with graphite electrodes of sandwich type, and the electric conductivity was measured using an apparatus designed in our laboratory⁷ and electrometer with a vibration

capacitor Femtometer 475 B (Victoreen) at the input. During the measurement the measuring cell was filled with argon.

RESULTS AND DISCUSSION

Formation of the complexes in solution was accompanied by a blue coloration, the original DABCO and quinone solutions being colourless and yellow, respectively. Absorption spectra of DABCO-chloranil and DABCO-bromanil complexes in benzene and tetrahydrofuran are given in Fig. 1. All the spectra contain an absorption band in the region of 600 nm. It was found by the Job's method that the both complexes have the donor-acceptor molar ratio 1 : 1. Absorption bands at 426 and 450 nm (Fig. 1, curve 2) of the DABCO-chloranil system correspond to the chloranil anion-radical⁸⁻¹⁰. Results of the EPR measurements confirmed the presence of ion-radicals in the studied systems, too. Fig. 2 gives EPR spectra of the systems DABCO-chloranil and DABCO-bromanil in benzene and tetrahydrofuran. The spectra are symmetrical simple lines with $g = 2.006 \pm 0.001$. Position of the lines corresponds to anion-radicals of chloranil¹¹ and bromanil, respectively. From the figure it is also obvious that the EPR signal intensity is the higher the more polar is the solvent,

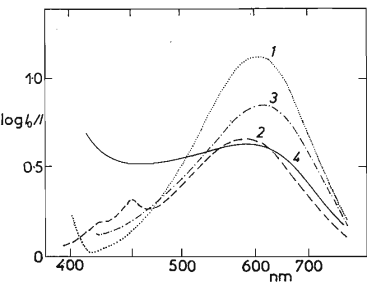


FIG. 1

Absorption Spectra of Complexes DABCO-Chloranil (1 : 1) and DABCO-Bromanil (1 : 1) in Benzene and Tetrahydrofuran

Initial concentrations of the donor and the acceptor are $5 \cdot 10^{-2} M$. Curve 1, DABCO-chloranil in benzene; 2 DABCO-chloranil in tetrahydrofuran; 3 DABCO-bromanil in benzene; 4 DABCO-bromanil in tetrahydrofuran.

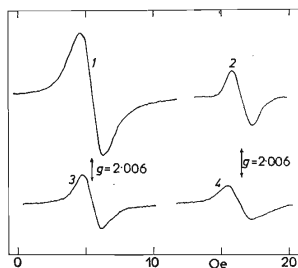
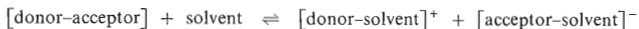


FIG. 2

EPR Spectra of Complexes DABCO-Chloranil (1 : 1) and DABCO-Bromanil (1 : 1) in Benzene and Tetrahydrofuran

Initial concentrations of the donor and the acceptor are $5 \cdot 10^{-2} M$. Curve 1 DABCO-chloranil in tetrahydrofuran; 2 DABCO-chloranil in benzene; 3 DABCO-bromanil in tetrahydrofuran; 4 DABCO-bromanil in benzene.

i.e. number of ion-radicals in the system is greater. Higher number of ion-radicals in a more polar solvent is due to dissociation of the complex according to the following scheme¹²:



Absorption spectra of the systems DABCO-chloranil in benzene and DABCO-bromanil in benzene and tetrahydrofuran do not contain any bands corresponding to chloranil or bromanil anion-radicals, in spite of that EPR detects their presence (Fig. 2, curves 2-4). This fact can be explained by the EPR apparatus being able to record lower ion-radical concentrations than spectrophotometer.

Increased dissociation of the complexes into ion-radicals in tetrahydrofuran made it possible to determine the stoichiometric composition of the complexes from the dependence of electric conductivity on the donor to acceptor molar ratio^{13,14}. The maximum conductivity was observed at the ratio 1 : 1, which confirmed the stoichiometric composition of the complex.

The solid complexes DABCO-chloranil and DABCO-bromanil exhibit a semiconductor character and are paramagnetic. Their EPR spectra were simple asymmetrical lines in the region $g \approx 2$. The EPR lines asymmetry indicates an interaction of unpaired spin with a crystalline field¹⁵. However, the EPR signals intensity was relatively low, being of the order of one unpaired spin per 10^5 molecules of the complex. Origin of the unpaired spins in these complexes in solid phase must be ascribed rather to impurities and lattice defects and not to ion-radical character of the complexes¹⁶⁻¹⁹.

Resistivity of the solid polycrystalline compressed samples of DABCO-chloranil and DABCO-bromanil complexes is $2.3 \cdot 10^{12} \Omega \text{ cm}$ and $4.3 \cdot 10^{10} \Omega \text{ cm}$, respectively (in argon at 22°C). The electric conductivity activation energy of the complexes calculated from the temperature dependence of conductivity $\sigma = \sigma_0 \exp(-E_a/kT)$ (ref.³) is 0.56 and 0.60 eV, respectively. Resistivity of the complexes in air was lower than that in argon by 1 to 2 orders of magnitude, *viz* $7.4 \cdot 10^{10} \Omega \text{ cm}$ and $2.6 \cdot 10^9 \Omega \cdot \text{cm}$ in the case of DABCO-chloranil and DABCO-bromanil, respectively. Higher conductivity in air is probably due to humidity, since DABCO with water forms very easily stable monohydrate^{1,20}.

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