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Direct Determination of Charge Transfer Energy

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The absorption spectrum of the gaseous anthracene - chloranil complex was measured. The Coulomb energy contributing to the charge-transfer transition was determined to be 3.03 eV. The polarization energy for the transition was 0.17 eV in an *n*-heptane solution.

Since the charge-transfer theory was advocated by Mulliken, various theoretical and experimental investigations have been made of the charge-transfer complexes.[1,2] By means of the theory, approximate linear relations between the energy of the charge-transfer transition and the ionization potential of the donor or the electron affinity of acceptor have been derived and experimentally confirmed.[3,4]

According to McConnell *et al.*, the energy of the charge-transfer transition, W, can often be expressed simply by the following relation:[5]

$$W = I - A - C - P \qquad (1)$$

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where I is the energy required to take an electron out of the highest occupied molecular orbital of a donor and where A is the energy gained as an electron is brought to the lowest vacant molecular orbial of an acceptor. C is a Coulomb-energy term, and P is a polarization-energy term.

If the geometrical configuration of the complex is known, the Coulomb term can be calculated by the following equation:[6]

$$C = \int \phi^2(1)\frac{e^2}{r_{12}}\theta^2(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \qquad (2)$$

where ϕ is the molecular orbial of a donor and θ is that of an acceptor. However, the polarization energy is rather difficult to estimate theoretically, as it depends on the properties of the solvent as well as on the geometry of the complex. Moreover, the electron affinity of the acceptor can not be obtained accurately.

Because of these ambiguities, the estimation of Eq. (1) is very difficult as long as the available data are restricted to the optical absorption in condensed phases. Fortunately, the electron affinity of chloranil has recently been determined by the magnetron method to be 2.45 eV.[7] In order to make a rigorous analysis of each term in Eq. (1), we tried to observe the gaseous absorption spectrum of the anthracene-chloranil complex. The ionization potential of anthracene was determined to be 7.38 eV by the photoionization method.[8]

Experimental

Anthracene used in this work was a synthetic and zone-refined material prepared by Iwashima.[9] Chloranil was purified by recrystallization from benzene. The n-heptane solution of the anthracene - chloranil complex was prepared by mixing equimolecular components to an appropriate concentration.

The optical data for the complex in the gas phase were obtained by means of an Aminco 4-8401 monochromator. Anthracene and equimolecular chloranil were placed in a Pyrex-glass cell 30 cm long; the cell was sealed off after evacuation. The vapour pressure of chloranil is very low, so the cell was heated to around 250°C in a 50-kW electric furnance.[10] The absorption spectrum of the gaseuous complex was measured rapidly with a 200-W tungsten lamp.

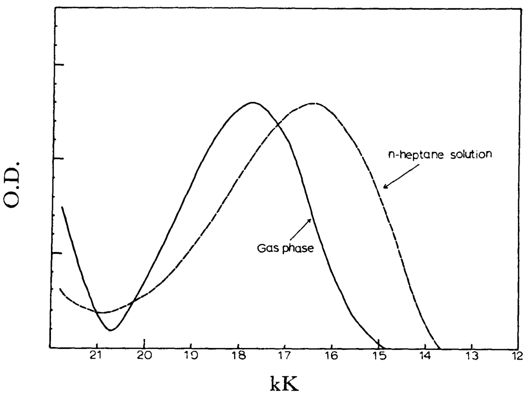

Fig. 1. Absorption spectra of the anthracene-chloranil complex.

Results and Discussion

Figure 1 shows the absorption spectrum of the anthracene - chloranil complex in the gas phase. The solution spectrum in n-heptane is added for the sake of comparison. Heptane was chosen as a common inert solvent in view of its solvent effect.[11]

The complex vapour gave evidence of a charge-transfer absorption maximum at 17800 cm^{-1} as compared with a value of 16400 cm^{-1} in an n-heptane solvent.

The shapes of the charge-transfer bands in the gaseous state and in solution are almost the same; the bands are all broad and diffuse. The asymmetry of bands is preserved in the vapour. However, the half-width, δ, in the gas phase is considerably smaller than that in solution (*e. g.*, δ=3060 cm^{-1} in gas and δ=3930 cm^{-1} in solution). The wave-number-shift from gas to solution amounts to 1400 cm^{-1} in this complex; this is considerably smaller than those in the complexes with TCNE.[11]

It has been shown that the width and diffuseness of the charge-transfer bands result from the difference in the form of the potential curves for the ground and excited states of the complex.[12] Therefore we tried to estimate the location of the 0–0 band with the aid of the fluorescence spectra, since the spectrum for the anthracene complex is deficient, but our efforts were in vain. Therefore, by analogy with the general behaviour of the mirror points of the fluorescent chloranil complexes, the 0–0 band of the anthracene - chloranil was estimated to be at 15400±300 cm^{-1}, which is equivalent to 1.91 eV.[2]

As a considerable amount of the change in the molecular coordinate is caused by the augmentation of the Coulomb energy in the excited state,

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the 0–0 position generally shifts to the band edge of the charge-transfer transition. Therefore, it is understandable that the band width of the absorption spectrum is often broader than that of the fluorescence.[2]

In 1964, Chakrabarti *et al.*,[13] using the relation concerning the solvent shifts, estimated the location of the band maximum of gaseous anthracene-chloranil at 21000 cm^{-1}. This overestimated value may be due to the misapplication of the solvent effect. They also failed to explain the dipole moment in the ground state.

In a previous paper,[11] we ourselves have reported the gaseous absorption spectra of aromatic-TCNE complexes. We concluded that the charge-transfer bands obey the McRae's formula of solvent effect, so the gas phase spectra can be regarded as the origin of that effect. This implies that the charge distribution of the complex is nearly preserved in normal solvents and in the gas phase.

Presupposing that this theory is valid for the anthracene-chloranil complex, we will proceed in our discussion. In the first place, the Coulombic-attraction term contributing to the charge-transfer transition can be directly deduced from Eq. (1), as the polarization energy vanishes in the gas phase. Therefore, the Coulomb term of the anthracene-chloranil amounts to 3.03 eV. It is a quite reasonable value compared with those calculated for a series of aromatics-TCNE complexes (*e. g.*, 3.34 eV for the naphthalene-TCNE, 3.10 eV for the pyrene-TCNE, and 2.91 eV for the perylene-TCNE).[14] These calculations have been made on every configuration, using Eq. (2) with the point-charge approximation. In view of their origin, the constancy of these attraction terms among various complexes is quite natural.

Employing the calculated Coulomb energy, we shall now determine the electron affinity of TCNE again. The ionization potential of naphthalene is 8.12 eV.[15] As the transition energy of the naphthalene-TCNE complex is considered to be around 2.23±0.05 eV, its electron affinity can be estimated as 2.55 eV. This value is in good agreement with the 2.60 eV assumed in the previous paper.[11]

The smaller affinity was also estimated to be 2.10 eV from the SCFMO calculations performed by Flurry's laboratory.[16] The value derived by Briegleb from the spectroscopic data, 1.80 eV, seems too small.[17]

As to the polarization energy term, we define the spectral shift in the condensed phase as the polarization energy.

Table 1. The results of the charge transfer energies (eV)

	Anthracene-chloranil	Naphthalene-TCNE
Ionization potential of donor	7.38	8.12
Electron affinity of acceptor	2.45	2.55±0.05
Coulomb energy	3.03±0.05	3.34
Polarization energy		
in *n*-heptane	0.17	0.29
in carbon tetrachloride	0.22	0.38

So far, the physical meaning of the polarization energy has been very obscure, since the difference between the absorption maximum and the theoretically-calculated transition energy is considered to be the energy. This term often grows to 1 eV, depending on the MO adopted.[6] According to our definition, the transition energies of the anthracene-chloranil are 0.17 eV in *n*-heptane and 0.22 eV in carbon tetrachloride. Those of the naphthalene-TCNE are 0.29 eV in *n*-heptane and 0.38 eV in carbon tetrachloride.[11] (Summarized in Table 1) Consequently, the dipole-polarization force acting on the charge-transfer transition of the naphthalene-TCNE is stronger than that of the anthracene-chloranil by a factor of 1.7. This quantity can be explained by the usual McRae's formula.[18]

In the above treatment, we neglected an ionic character of several percent which stabilizes the complex in the ground state.[19] Probably, it influences each term in Eq. (1) within an accuracy of 0.20 eV. In the case of the TCNE complex, this effect may contribute to the increase in the electron affinity of TCNE, since its ionicity is considerably stronger than that of the chloranil complex.[19]

For further investigations of the charge-transfer complex, it is desirable to determine wavefunctions such as we obtained in this experiment wihch will accurately reproduce the energy diagram.

Giacometti *et al.*, who first treated the chloranil complex theoretically, adopted a complex with *p*-phenylenediamine in their MO calculations.[20] The SCFMO approach to the molecular complex system also seems fruitful.[21]

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