Absorption Spectra of Gaseous Charge-Transfer Complexes Aromatics-TCNE

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Recently, several articles have appeared on charge-transfer complexes in the gas phase.1−3) So far, however, this interest has been confined to volatile complexes with high vapour pressures. We here present a preliminary report of some vapour-phase studies of less volatile complexes such as TCNE (tetracyanoethylene) complexes with aromatic hydrocarbons.

Spectrophotometric measurements were made using an Aminco 4-8401 monochromator, to which was attached an absorption cell 7 cm in length. It was maintained at about 200°C within an electric oven.

Characteristic charge-transfer bands were observed in the near-ultraviolet and visible regions. As a typical example, the bands for the napthalene-TCNE complex were located at 21.1 kK and 26.3 kK; these are blue shifts of 3.1 kK and 3.3 kK respectively from those found when the complex is dissolved in carbon tetrachloride. No marked change in shape was observed between the gas and condensed phases. The gas and solution data are compared in Table 1.

TABLE 1. THE CHARGE-TRANSFER BANDS OF AROMATICS-TCNE COMPLEXES

Donor	Gas phase kK	CCl_4 solution kK	Gas-to-solution shift kK
Naphthalene	21.1	18.0	−3.1
	26.3	23.0	−3.3
Durene	20.6	19.2	−1.4
Diphenyl	22.2	20.0	−2.2
	28.6	25.7	−2.9
Pyrene	13.5	14.0	+0.5
	16.5	20.5	+4.0
	23.0	25.8	+2.8
Stilbene	13.4	16.8	+3.4
	21.1	26.0	+4.9

It is noteworthy that, for naphthalene-TCNE complex, the higher energy component is affected to a greater extent; this shows the same tendency as the pressure effect in a methylene chloride solution.4)

The solvent sensitivity of the charge-transfer bands stands in marked contrast to those of ordinary transitions. Many factors, such as solvent-solute interactions, may contribute to the spectroscopic effects.

According to Bayliss and McRae,5) when the solute dipole moment increases as a result of a transition, the contribution of the dipole-polarization forces (the polarization of solvent molecules by the solute dipole) to the solvation energy is increased, thereby giving a gas-to-solution red shift.

In the naphthalene-TCNE complex the dipole moment is 1.28D in the ground state6) and is assumed to be 10—15D in the excited state.7)

Qualitatively the spectra are interpreted by assuming that, on this shift, the polarization red shift is superimposed, and that the resultant shift is to the longer-wavelength region.

However, the molecular complexes in the solution should be considered as three-component systems including solvent molecules, which not only influence the dipole-polarization forces, but also change the conformations of the complexes. Thus, the interpretation of the results of several individual effects is made difficult because of the lack of quantitative information.

The results for other TCNE complexes are also listed in Table 1. Some of them show different solvent effects; these are now under consideration. Attempts to determine the formation constants and thermodynamic constants were unsuccessful, for these complexes were unstable at high temperature and easily decomposed.

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1) F. T. Long and R. L. Strong, *J. Am. Chem. Soc.*, **87**, 2345 (1965).

2) J. Prochorow and A. Tramer, *J. Chem. Phys.*, **44**, 4545 (1966).

3) M. Tamres and J. M. Goodenow, *J. Phys. Chem.*, **71**, 1982 (1967).

4) J. R. Gott and W. G. Maisch, *J. Chem. Phys.*, **39**, 2229 (1963).

5) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

6) G. Breigleb, J. Czekalla and G. Reuss, *Z. Physik. Chem.* (Frankfurt), **30**, 333 (1961).

7) J. Czekalla and K. O. Meyer, *ibid.*, **27**, 185 (1961).