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STUDIES ON THE WEAK CHARGE-TRANSFER INTERACTIONS OF NITROBENZENE WITH ANILINE AND N,N-DIMETHYLANILINE

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Abstract—The weak intermolecular charge-transfer interactions of nitrobenzene with aniline and N,N-dimethylaniline were studied by optical methods. It is suggested that the CT absorption of the aniline–nitrobenzene system is mainly due to loose contact pairs, but the presence of a slight amount of true complex is also present. The equilibrium constant K_c for complex formation for the N,N-dimethylaniline–nitrobenzene system was evaluated. The effects of polar solvents such as ethanol and acetone on the CT absorptions were studied. For the N,N-dimethylaniline–nitrobenzene system it was found that CT absorption was also caused by loose contact pairs as well as true complexes. The contact CT interaction was inhibited by solvation of the donor or acceptor molecules by polar solvents.

INTRODUCTION

SINCE NITROBENZENE is not usually a strong acceptor in charge-transfer complexing, one may expect very weak charge-transfer interactions between nitrobenzene and donors such as aniline and its derivatives. In fact, when nitrobenzene is added to aniline or N,N-dimethylaniline, the mixtures show an orange colouration, indicating the appearance of CT absorption. Dale *et al.*[1] reported that the equilibrium constant for complex formation between N,N-dimethylaniline and nitrobenzene was 0·4 l/mole in cyclohexane at 20°, whereas that for the aniline–nitrobenzene system was immeasurably small. Hence contact CT interaction is expected to occur in the latter system.

For weak molecular complexes, reliability of equilibrium constant values (K_c) evaluated by the use of the Benesi–Hildebrand equation[2] has been widely discussed.[3–6] It has been found that for some electron donor-acceptor systems the calculated equilibrium constants depend on the wavelength of measurement. Thus, Johnson and Bowen[3] found a variation of K_c with wavelength for the TCNE–naphthalene system, which interpreted by postulating the presence of 1:2 or 2:1 complex along with a 1:1 complex. However, the significance of a ternary complex is in doubt[5,7] and the variation of K_c is considered to be attributable to the deviation from Beer's law of the complex absorption.[4,5]

In this paper, characteristics of weak intermolecular CT interactions of nitrobenzene with aniline and N,N-dimethylaniline are studied by optical methods.

RESULTS AND DISCUSSION

The absorption spectra of aniline–nitrobenzene and N,N-dimethylaniline–nitrobenzene systems in cyclohexane are shown in Fig 1, where the absorption for the same concentration of nitrobenzene is presented for comparison. It is seen that

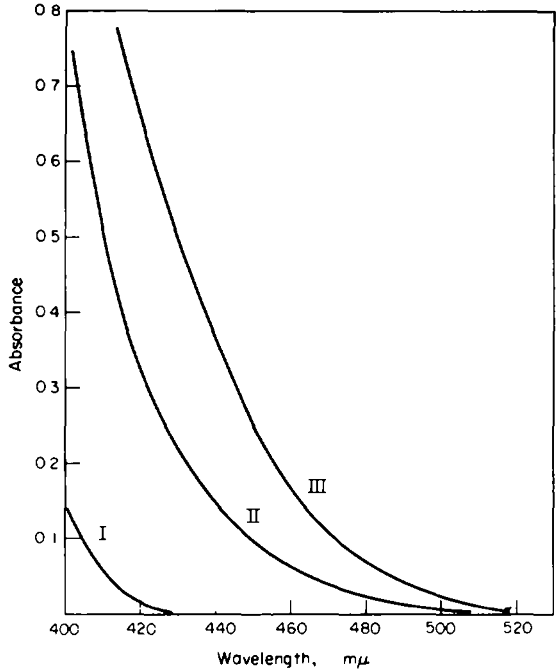

FIG 1. Absorption spectra in cyclohexane. I: Nitrobenzene 1·62 × 10^{-2} mole/l, II: aniline 0·967 mole/l + nitrobenzene 1·62 × 10^{-2} mole/l, III: N,N-dimethylaniline 0·743 mole/l + nitrobenzene 1·62 × 10^{-2} mole/l

although no absorption maximum of a band appears in the wavelength range observed, an apparent shift of the absorption curve to longer wavelengths is seen for each system as compared with the absorption curve of nitrobenzene. This seems to indicate that a very weak CT interaction occurs in each system, since similar spectral

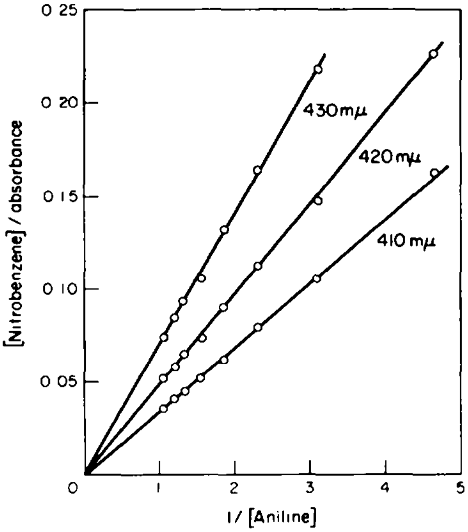

FIG 2. Benesi–Hildebrand plot for the aniline–nitrobenzene system in cyclohexane at 20°

changes have been observed for a number of electron donor-acceptor systems which have small equilibrium constants for complexing or have no true complex but loose contact pairs.[8–11] Therefore, the extra absorptions appearing in the visible region are considered to be due to intermolecular CT transitions. That the more striking spectral change is observed for the N,N-dimethylaniline system than for the aniline system is likely to give support to the above interpretation in view of the ionization potentials of N,N-dimethylaniline (7·3 eV) and aniline (7·7 eV). Moreover, in connection with the present intermolecular CT bands, an intramolecular CT band has been found in the tail of the long wavelength $\pi-\pi^*$ absorption of 4-hydroxy (or amino),4′-nitrodiphenylmethane.[12]

The Benesi–Hildebrand plot for the CT absorption of the aniline–nitrobenzene system at 410, 420 and 430 mμ gave a linear relationship between 1/[Aniline] and [Nitrobenzene]/Absorbance, and the straight lines obtained by the least-squares method could be approximately extrapolated to the origin of the coordinates as shown in Fig 2. This may imply that the equilibrium constant (K_c) for complex formation is very nearly zero. So, one would deduce that no true complex was formed between aniline and nitrobenzene but only a contact CT interaction[13] occurred in this system. However, it should be noted that sometimes little reliance can be placed upon small K_c values determined from optical measurements.

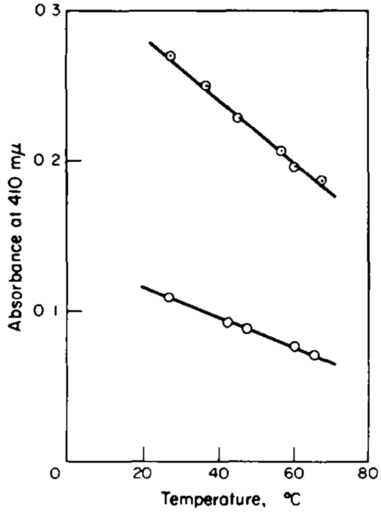

FIG 3. Temperature dependence of the absorption intensities in cyclohexane. ○: Aniline 6·4 × 10^{-2} mole/l + nitrobenzene 5·8 × 10^{-2} mole/l, ⊙: N,N-dimethylaniline 6·2 × 10^{-2} mole/l + nitrobenzene 5·8 × 10^{-2} mole/l

According to Tsubomura and Mulliken,[14] the contact CT absorption was essentially temperature independent. In the case of the aniline–nitrobenzene system, the absorption intensity at 410 mμ decreased appreciably on increase of temperature from 26° to 65° (Fig 3) as found in the N,N-dimethylaniline–nitrobenzene system which has the apparent K_c value shown later. The observed decrease in absorption intensity cannot be explained by thermal expansion of the solution, that is, the absorbance of this system at 410 mμ at 26° is 0·108 and decreases at 65° by about 34%. Therefore, this may be attributed to a finite enthalpy of interaction between aniline and nitrobenzene.

The concentration of the contact pair [D··A] is expressed as

$$[D\cdots A] = \alpha[D][A]$$

where [D] and [A] are the concentrations of donor and acceptor, and α is the number of average possible contact sites for a donor molecule around any acceptor molecule.[13] When a system contains donor and acceptor in equal concentration, [D] = [A], this equation can be written as

$$[D\cdots A] = \alpha[D]^2 = \alpha[A]^2$$

and absorbance at a given wavelength for a 1 cm light path length is expressed by the quadratic equation for [D] or [A],

$$\text{Absorbance} = \alpha'[D]^2 = \alpha'[A]^2$$

where α' is $\alpha \times \varepsilon$ and must be independent of [D] or [A]. We examined the validity of this equation for the aniline–nitrobenzene system. The results are shown in Fig 4. It is clearly seen that the value of α' depends on the concentration. This experimental observation together with the temperature dependency of the CT absorption may indicate that even in the aniline–nitrobenzene system there is a slight amount of complex besides the loose contact pairs.

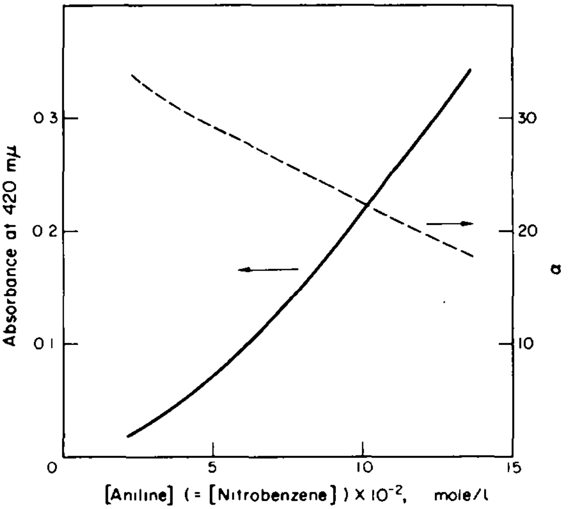

FIG 4. Changes in absorption intensity and the α' value of the [aniline] = [nitrobenzene] system by dilution with cyclohexane

Next we deal with the N,N-dimethylaniline–nitrobenzene system. In order to apply the Benesi–Hildebrand equation, generally the donor concentration should be much higher than the acceptor concentration. But it should be noted that there is a

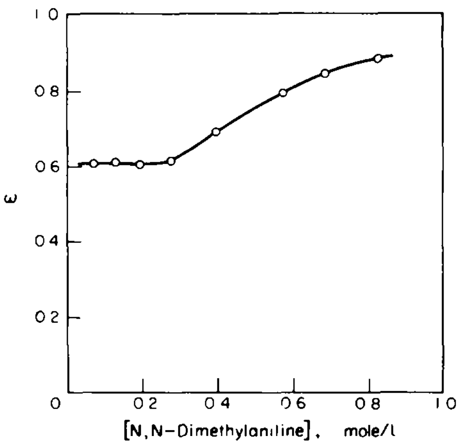

FIG 5. Concentration dependence of ε (at 334 mμ) of N,N-dimethylaniline in cyclohexane

possibility of some interactions between the polar donor molecules in a solution of high concentration. As for N,N-dimethylaniline it has been revealed by dipole moment measurements that it associates to give the dimer in cyclohexane (K_c = 0·55 l/mole at 25°).[15] Accordingly we measured the absorption of N,N-dimethylaniline in cyclohexane at various concentrations and determined the concentration range in which the absorption obeyed Beer's law. As may be seen from Fig 5, the molar extinction coefficient depends on the concentration in the region higher than 0·3 mole/l, indicating that Beer's law holds only in concentrations lower than 0·3 mole/l. Therefore, the Benesi–Hildebrand equation must be applied

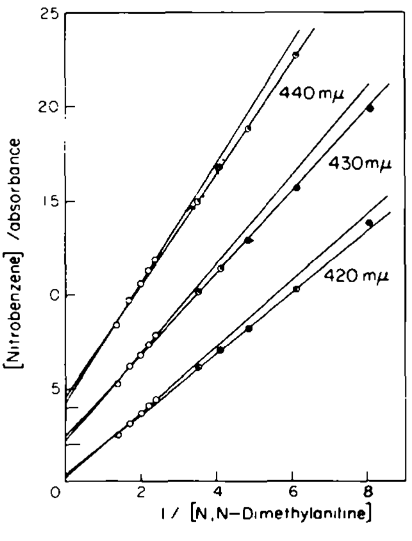

FIG 6. Benesi–Hildebrand plot for the N,N-dimethylaniline–nitrobenzene system in cyclohexane at 22°. ○: [donor] > 0·3 mole/l, ⊙: [donor] < 0·3 mole/l. The zero levels of the ordinate for the results observed at 430 and 440 mμ are moved upwards

TABLE 1. THE EQUILIBRIUM CONSTANT (K_c IN l/mole) OF THE N,N-DIMETHYLANILINE–NITROBENZENE COMPLEX EVALUATED AT 420, 430 AND 440 mμ

Wavelength	[D]* <0·3 mole/l	[D]* >0·3 mole/l
420 mμ	0·22	0·085
430 mμ	0·22	0·081
440 mμ	0·21	0·082
Averaged	0·22	0·083

* The concentration of N,N-dimethylaniline. The concentration of nitrobenzene: 1·62 × 10^{-2} mole/l. Solvent: cyclohexane. Temperature: 22°.

separately to the solutions in which the donor concentrations are higher and lower than 0·3 mole/l. The Benesi–Hildebrand plots for both solutions gave linear relationships between 1/[Donor] and [Acceptor]/Absorbance as shown in Fig 6. From the straight lines obtained by the least-squares method, the apparent K_c values were obtained. The results are presented in Table 1.

In the present case, it can be said that the K_c values calculated at several wavelengths are almost constant within the experimental error and thus are independent

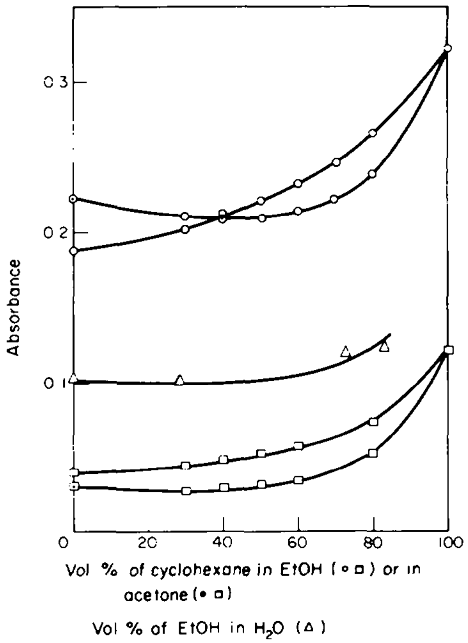

FIG 7. Solvent effect on the CT absorptions. ○ ⊙: N,N-Dimethylaniline 0·66 mole/l + nitrobenzene 9·75 × 10^{-3} mole/l, observed at 430 mμ. □ ▣: Aniline 0·859 mole/l + nitrobenzene 9·75 × 10^{-3} mole/l, observed at 430 mμ. △: Sodium *p*-aminobenzenesulfonate 4·2 × 10^{-2} mole/l + sodium *m*-nitrobenzenesulfonate 4·6 × 10^{-2} mole/l, observed at 410 mμ

of wavelength. However, the K_c value for the solution of higher concentration of the donor is considerably smaller than that for the solution of lower concentration. The smaller value of K_c may be attributed to an interaction between the N,N-dimethylaniline molecules, probably the dimerization as reported by Philippe *et al.*,[15] which is in competition with complex formation. In the case of the higher concentration system, the contact CT interaction is considered to occur as well as complexing. In fact, as shown below, the CT absorption of this system showed a similar solvent effect with that of the aniline–nitrobenzene system in which the contact CT interaction was predominant as seen above.

Effects of polar solvents on the CT absorptions were examined using EtOH and acetone. As seen from Fig 7, the absorbances at a given wavelength were clearly reduced on adding EtOH or acetone to the cyclohexane solutions. This seems to indicate that the CT band of each system is either shifted to higher energies or decreased in intensity, or both. Hence it can be said that polar solvents hinder the CT interactions for the present systems. In the case of the aniline–nitrobenzene system, polar solvents seem to play a role in preventing effective contact between the donor and the acceptor molecules. The change in viscosity of the solvents and the occurrence of solvation of the interacting molecules would be possibly accounted for by the change in the number of the effective encounter collisions. However, the observed change in the CT absorption cannot be interpreted in terms of the viscosity solvents, because the viscosity of acetone (0·322 cP at 20°) is smaller than that of cyclohexane (0·97) and EtOH (1·19). Thus we must take into consideration the effect of solvation. In the present solvent effects, the hydrogen bonding between the solute and solvent is considered not to be a predominant factor, because acetone is not able to form a hydrogen bond with N,N-dimethylaniline or nitrobenzene.

Davis and Symons[16] found that the CT band shifted to shorter wavelengths on adding MeOH to a solution of the hexamethylbenzene–chloranil complex in CCl_4 and they discussed it in terms of solvation. In the case of the contact CT interaction, the solvated donor and/or acceptor molecules are considered to be unable to cause adequate contact to give rise to the CT absorption. It is seen from Fig 7 that the N,N-dimethylaniline–nitrobenzene system shows a similar solvent effect to the aniline–nitrobenzene system. Hence it is deduced that in the former system, in which the donor concentration is 0·66 mole/l, the absorption is almost due to the loose contact pairs.

It is suggested here that the contact CT interaction is hindered by solvation by polar solvents. So, we can expect that when the sodium sulfonate group is introduced to aniline and nitrobenzene the contact CT absorption of the sodium sulfonate derivatives is reduced by addition of H_2O to the EtOH on account of the hydrophilic property of this group. The results shown in Fig 7 are in accord with this expectation.

EXPERIMENTAL

Materials. All materials were obtained commercially. Aniline was purified by refluxing with Zn powder and distilling; b.p. 185°. N,N-Dimethylaniline was distilled: 43°/1 mm. Nitrobenzene was shaken with dilute H_2SO_4 and distilled: 62°/4 mm. Sodium *p*-aminobenzenesulfonate and sodium *m*-nitrobenzenesulfonate were recrystallized repeatedly from water. Cyclohexane, EtOH and acetone were purified by standard procedures.

Measurements of absorption spectra. Absorption spectra were measured with a Shimadzu Spectrophotometer QV-50 using 1 cm quartz cells. For temperature dependence experiments, the cell box was maintained at constant temperature by passing water from a constant temperature bath through the cell box.

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