Charge-Transfer Complexes of Trinitrobenzene with Tetramethyl-p-phenylenediamine and p-Dimethoxybenzene

By Suehiro IWATA, Hiroshi TSUBOMURA* and Saburo NAGAKURA

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Charge-transfer molecular complexes[1] between 1, 3, 5-trinitrobenzene (abbreviated hereafter to TNB) and some donor molecules have been studied very extensively.[2] For example, Foster and Thomson reported that the tetramethyl-*p*-phenylenediamine - TNB complex shows the charge-transfer absorption at 614 mμ in acetonitrile and at 583 mμ in cyclohexane, and that this complex is dissociated into ions in water and methanol.[3] Thus far, however, no quantitative consideration of the equilibrium constants and the heats of formation of this complex has been made.

In the present paper spectroscopic studies have been carried out with tetramethyl-*p*-phenylenediamine - TNB and *p*-dimethoxybenzene - TNB complexes, and the equilibrium constant and the heat of formation have been determined. Consequently, it has been found that the tetramethyl-*p*-phenylenediamine complex has the largest heat of formation and the longest wavelength charge-transfer absorption band among the TNB complexs studied so far.

Experimental

Materials. — TNB and *p*-dimethoxybenzene were purified by recrystallizing them from ethanol; their melting points were 120°C and 54.5°C, respectively. Tetramethyl-*p*-phenylenediamine (abbreviated hereafter to TMPD) was obtained by neutralizing its hydrochloride, and it was purified by vacuum sublimation.

n-Heptane was shaken with concentrated sulfuric acid, then washed with water, dried with calcium chloride and thereafter with sodium, and finally fractionally distilled.

Measurements.—A Cary recording spectrophotometer, model 14, was used for the measurements of the ultraviolet and visible absorption spectra. These spectra were measured by using cylindrical cells of 10 cm. light path length made of fused silica. The donor and the acceptor solutions, which were separately prepared, were mixed with each other just before the absorption measurements. For the experiments of the temperature dependence of the absorption intensity, we used a cell box with a heater, controlling the temperature with a thermister.

Results and Discussion

TMPD-TNB Complex.—The mixed solution of TMPD with TNB was violet. The absorption spectrum of this colored solution is shown in Fig. 1. The absorption maximum appears at 620 mμ (2.0 eV.). This absorption band may be thought to be Mulliken's charge-transfer band characteristic of the 1 : 1 molecular complex between TMPD as an electron donor and TNB as an electron acceptor. In order to make sure of this point and to evaluate the equilibrium constant for this system, Benesi-Hidebrand's equation[4] was applied.

Since, in the present experiments, the concentration of TMPD was much larger than that of TNB,[5] Benesi-Hildebrand's equation is applicable:

$$\frac{1}{\varepsilon^*}=\frac{C_a l}{D}=\frac{1}{K\varepsilon}\,\frac{1}{C_d}+\frac{1}{\varepsilon} \qquad (1)$$

where C_a and C_d are the initial concentrations

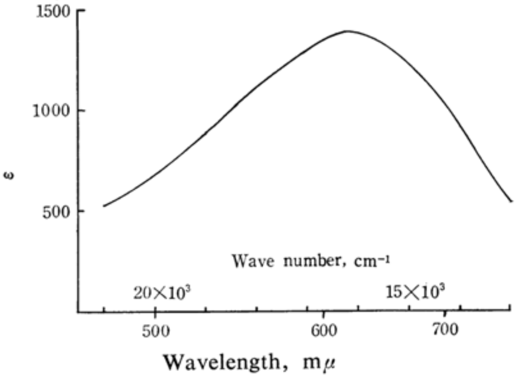

Fig. 1. The visible absorption spectrum of the molecular complex between TMPD and TNB in *n*-heptane (at 30°C).

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* Present address: Faculty of Engineering Science, Osaka University, Toyonaka, Osaka.

[1] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

[2] G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer - Verlag, Berlin - Göttingen - Heidelberg (1961).

[3] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).

[4] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[5] The initial concentrations of TNB and TMPD actually taken in the present experiment are 2.81~2.99×10⁻⁴ mol./l. and 5~20×10⁻³ mol./l. respectively.

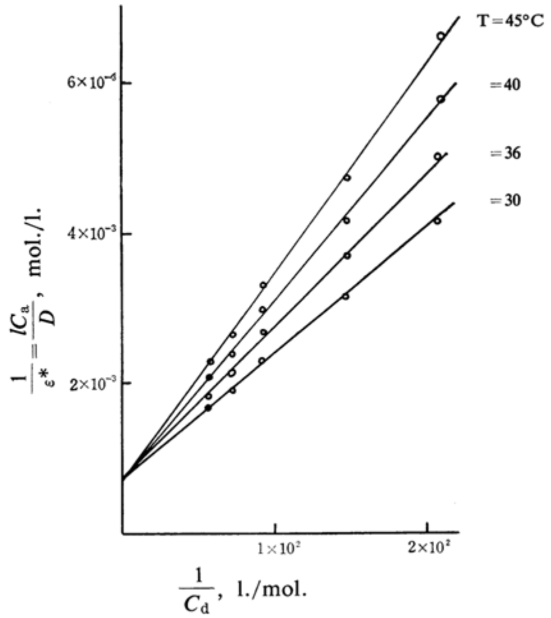

Fig. 2. Benesi-Hildebrand's plots for the TMPD-TNB system in *n*-heptane at various temperatures. Optical densities are measured at 620 mμ.

of the electron donor and acceptor respectively; K, the equilibrium constant for the 1 : 1 complex formation; D, the absorbancy; ε, the molar extinction coefficient, and l, the light path length of the cell. As may be seen in Fig. 2, a straight-line relationship is completely satisfied between $1/\varepsilon^*$ and $1/C_d$. This means that the 1 : 1 charge-transfer complex is formed between TMPD and TNB and that the charge-transfer band characteristic of the complex appears at 620 mμ. From the straight line obtained by the least-squares method, the equilibrium constant for the complex formation and the molar extinction coefficient of the charge-transfer band were determined by following the usual method.[4] The results obtained at 600, 620 and 640 mμ are given in Table I.[6]

Using the equilibrium constants at various temperatures given in Table I, we evaluated the heat of formation (ΔH) and the entropy change (ΔS) by the usual method.[7] The evaluated values are as follows:

$$\Delta H = -7.9 \text{ kcal./mol.} \qquad \Delta S = -18 \text{ e. u.}$$

These ΔH and ΔS values were the greatest of the known TNB molecular complexes. This seems to be closely related with the fact that the TMPD-TNB complex has a smaller transition energy of the charge-transfer band ($h\nu_{CT}$ =2.0 eV.) than do the other TNB complexes.

TABLE I. THE EQUILIBRIUM CONSTANT (K in l./mol.) AND THE MOLAR EXTINCTION COEFFICIENT (ε) OF THE TMPD-TNB COMPLEX EVALUATED AT 600, 620 AND 640 mμ

Temp. °C	K_{620}	K_{600}	K_{600}	Averaged	ε_{620}
30	44.4	42.8	44.4	43.9	1370
36	37.1	36.8	36.7	36.9	1340
40	29.3	30.0	29.2	29.5	1440
45	23.7	23.8	23.9	23.8	1520

Briegleb et al.[8] obtained the empirical formula of the relation between the ionization potentials (I) of the donor molecules and the transition energies of the charge-transfer bands ($h\nu_{CT}$) of TNB complexes:

$$h\nu_{CT} = I - 5.00 + \frac{0.70}{I-5.00} \tag{3}$$

From this relation and the observed $h\nu_{CT}$ value, the ionization potential of TMPD (I_{TMPD}) is evaluated to be 6.55 eV. A similar formula concerning chloranil complexes[8] leads to the I_{TMPD} value of 6.62 eV. It should be noticed that these two I_{TMPD} values are consistent with each other. Thus, it is concluded that TMPD has a small ionization potential and that in these two TMPD complexes the dative structure contributes largely to the ground state. This is related with the fact that TMPD complexes have a tendency to dissociate into ions in such polar solvents as methanol and acetonitrile.[3,9]

p-Dimethoxybenzene - TNB Complex. — The color of the mixed solution of *p*-dimethoxybenzene with TNB was yellow. The absorption spectrum ot this solution is given in

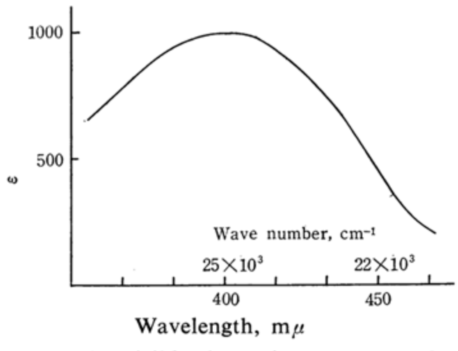

Fig. 3. The visible absorption spectrum of the molecular complex between *p*-dimethoxybenzene and TNB in *n*-heptane (at 22°C).

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[6] When, in the place of Eq. 1, the more precise Eq. 2 was used:

$$\frac{C_d}{\varepsilon^*} = \frac{lC_aC_d}{D} = \frac{1}{\varepsilon K} + \frac{1}{\varepsilon}(C_d + C_a) \tag{2}$$

K=43.9 l./mol. and ε=1370 (at 620 mμ and 30°C) were obtained. These values are consistent with the corresponding values obtained by Eq. 1.

[7] S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).

[8] Chapter VI of Ref. 2.

[9] W. Liptay, G. Briegleb and K. Schidler, *Z. Elektrochem.*, **66**, 331 (1962).

Fig. 3. The absorption band characteristic of the charge-transfer interaction between *p*-dimethoxybenzene and TNB appears at 400 mμ. By applying Eq. 1 to the absorbancy values measured at 420 mμ,[10] the equilibrium constant and the molar extinction coefficient were evaluated. The results are given in Table II.

From the temperature dependence of the equilibrium constants given in Table II, the heat of formation ($\varDelta H$) and the entropy change ($\varDelta S$) for the complex formation can be determined as follows:

$$\varDelta H = -3.2 \text{ kcal./mol.}$$

$$\varDelta S = -4.2 \text{ e. u.}$$

Furthermore, the molar extinction coefficient at the peak wavelength of the charge-transfer band could be evaluated as ~1000 by the aid of the equilibrium constant value obtained at 22°C.

TABLE II. THE EQUILIBRIUM CONSTANT (K) OF THE *p*-DIMETHOXYBENZENE-TEB COMPLEX EVALUATED AT 420 mμ

Temp., °C	19	22	25	28	31	36	40
K, l./mol.	3.5	3.3	3.1	2.9	2.8	2.5	2.3

By applying Eq. 3 to the peak wavelength of the charge-transfer band for the complex between *p*-dimethoxybenzene and TNB, the ionization potential of *p*-dimethoxybenzene could be obtained as 7.9 eV. This value is reasonable in view of the fact that the ionization potential of anisole has been determined as 8.2 eV. from the photoionization experiment of Watanabe.[11]

The Institute for Solid State Physics
The University of Tokyo
Azabu, Tokyo

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[10] The absorption maximum of the charge-transfer band is 400 mμ. In this wavelength region, however, there is a superposition of absorption due to TNB itself, so equilibrium constants are calculated by using the optical density at 420 mμ.

[11] K. Watanabe, *J. Chem. Phys.*, 26, 542 (1957).