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New Type of Charge-Transfer Complexes between Benzoic Acid 2-[(3,5-Dibromo-4-hydroxyphenyl)-3,5-dibromo-4-oxo-2,5-cyclohexadiene-1-ylidene)methyl]-ethyl Ester (TBPE) and Aliphatic Amines

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A study has been made of charge-transfer complexes formed between TBPE and aliphatic amines in nonpolar solvents. Large value of the equilibrium constant, large negative values of the heat of reaction as well as the reaction volume indicate that the complex of this type is very stable and the dative structure through hydrogen bonding is predominant.

Since the discovery of a charge-transfer complex(CTC) between iodine and benzene,1) a vast number of CTC's between electron donors and acceptors have been studied. During solvent-extraction studies of a variety of amines used as drugs, one of the authors (T. S.) has found that they react with TBPE to form complexes characterized by their remarkable thermochromic behavior in 1,2-dichloroethane.2-4) It was suggested that these complexes may be formed through hydrogen bonding between -O-H in TBPE and amino nitrogen. In this study, we have estimated thermodynamic parameters for the CTC formation and found that these complexes are of the new type as characterized by their strong CT band in the visible region, the large equilibrium constant, and the large negative values of the heat of reaction and reaction volume. As far as we are aware, no report for CTC's having all these properties has been put forward so far.

Triethylamine (TEA) and 2-(diphenylmethoxy)-N,N-dimethyl ethylamine (DHA) were chosen as representative aliphatic amines. Potassium salt of TBPE and HCl salt of DHA were converted to free TBPE and DHA. A toluene (benzene) solution of DHA or TEA (concentration of the order of 10^{-2} – 10^{-4} mol dm^{-3}) and that of TBPE (10^{-5} mol dm^{-3}) were mixed, and the electronic spectrum between 350 and 750 nm was recorded. The absorbances at the absorption maximum of the CT band were measured at various temperatures. No overlapping of the CT band with others was observed. The equilibrium constant and the molar absorptivity of the CT band at λ_{max} were estimated by means of the Benesi-Hildebrand plot1) assuming 1:1 complex. By means of the continuous-variations method the formation of the 1:1 complex was confirmed. The heat of reaction was estimated according to the van't Hoff plot (ln εK vs. 1/T).

A high-pressure vessel with sapphire windows was used, and the absorption spectra at various pressures were recorded on a spectrophotometer. The equilibrium constants in the logarithmic scale were plotted against external pressures and the plots were fitted by a computer program to the following quadratic equation:

$$\ln K_p/K_0 = ap^2 + bp + c \qquad (1)$$

where K_p and K_0 are the equilibrium constants at p and 0.1 MPa, respectively. The volume of reaction extrapolated to zero pressure was calculated by

$$bRT = -\Delta V - \kappa_T RT \qquad (2)$$

where κ_T denotes the isothermal compressibility of solvent used. The second term arises from the translational energy loss per mole upon complex formation (2.3 cm^3 mol^{-1} for toluene). In Table 1, the thermodynamic quantities are given.

Table 1. Thermodynamic parameters for the formation of TBPE–amine complexes at 25 °C

System	Solvent	K	ΔG°	ΔH°	ΔS°	ΔV°
		dm^3 mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	cm^3 mol^{-1}
TBPE–TEA	Toluene	18800	-24.4	-64.2	-134	-21.7
TBPE–DHA	Toluene	1960	-18.8	-48.2	-98	-18.2
TBPE–DHA	Benzene	1420	-18.0	-44.2	-88	-20.1

If the data in Table 1 are inspected, we notice some interesting points. (a) The K-values as well as -ΔH-values are remarkably large compared with those for usual CTC's. Therefore, this type of CTC is one of the most stable CTC's found so far, and is comparable with those between trialkylamines and iodine.5,6) However, the CT band of these compounds appears in the UV region. (b) The CT band appearing in the visible region is usually broad and the molar absorptivity small,7-9) while the CT band observed in this study is well-characterized and very strong (ε_{max}, 32300 for TBPE-DHA and 23700 for TBPE-TEA in toluene). (c) -ΔV = 14.1 cm^3 mol^{-1} for the formation of CTC between TCNE and hexamethylbenzene is probably the greatest value that appeared in the literature.10) It is notable that the -ΔV-values in Table 1 are considerably larger than this.

A remarkable red shift of the CT band with increasing solvent polarity was observed. For example, λ_{max} varies from 520 nm in CCl_4 to 590 nm in nitrobenzene. The shift is well correlated to the E_T-value,11) a solvent polarity parameter (Fig. 1). In more polar solvents such as acetone, a band due to TBPE anions appears at ca. 620 nm. This band can be distinguished from the CT band. In fact, both bands appear in an appropriate benzene–DMSO mixture. For aromatic amines of weak basicity, the CT band was not observed in the usual conditions. When so-called Proton Sponge is added to the benzene solution of TBPE, TBPE anions formed. Therefore, the conditions for the formation of CTC seem to depend on the basicity of amines as well as solvent polarity.

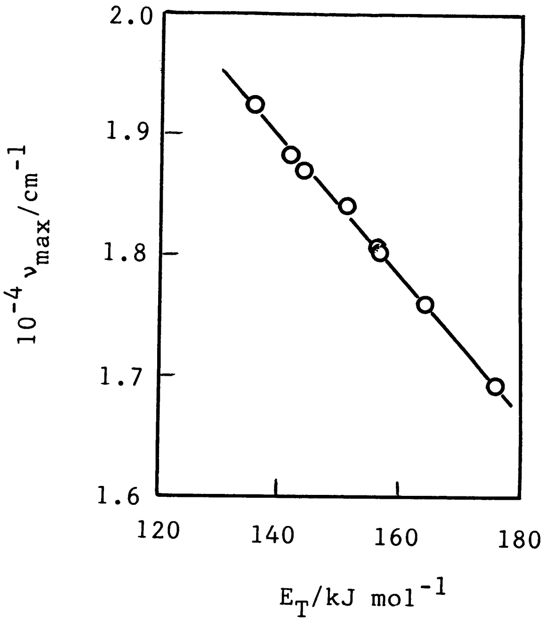


Fig.1. Relationship between ν_{max} and E_T.

Table 2. Comparson of the ^1H NMR δ-values (ppm) for the methylene and methyl protons in free amines, in their TBPE complexes, and in their HBr (HCl) salts in $CDCl_3$

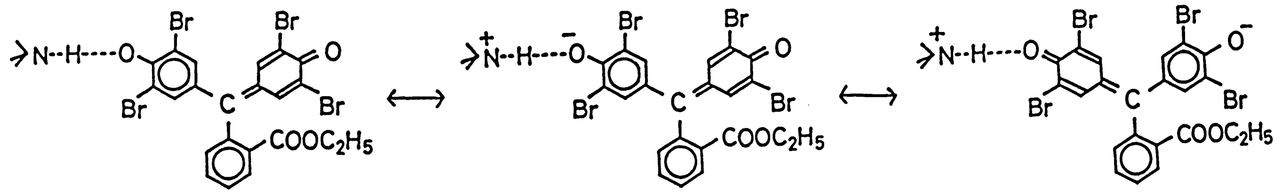
	$C\underline{H}_2$	$C\underline{H}_3$	Remark
TEA	2.42, q	0.98, t	
TEA-TBPE[a)]	3.00, q	1.28, t	$N-C\underline{H}_2-C\underline{H}_3$
TEA·HBr	3.18, q	1.42, t	
DHA	2.61, t	2.27, s	
DHA-TBPE[a)]	3.21, t	2.83, s	$O-CH_2-C\underline{H}_2-N(C\underline{H}_3)_2$
TMA·HCl[b)]	–	2.97, s	

a) These complexes were crystallized from a benzene solution.

b) DHA·HCl is sparingly soluble in $CHCl_3$. Data of trimethylamine (TMA) HCl salt are cited here.

In order to obtain further information of the nature of the complex, ^{1}H NMR spectra were recorded on a JEOL VRX 500 NMR spectrometer. The values of the chemical shift referred to TMS are given in Table 2. It is noted that the δ-values in the complex are close to those of salts, suggesting that the amino nitrogens are almost quaternary. Therefore, a strong H-bonding is probably involved. It has been clarified that hydrogen bond is not purely electrostatic in its origin but the CT force through H-bonding is involved.[12,13]

We propose therefore, that the CTC's observed in this work could be represented by the resonance hybrid of the H-bonded structure and the predominant dative structures as follows:



The above canonical resonance structures could be considered responsible for the large values of ε_{max}, the appearance of the CT band in the visible region, and the numerical values of the thermodynamic parameters.

References

1) H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc., 71, 2703 (1949).

2) T. Sakai, N. Ishida, and S. Turubo, Bunseki Kagaku, 28, 303 (1979).

3) T. Sakai, J. Pharm. Sci., 68, 875 (1979).

4) T. Sakai and N. Ohno, Analyst, 107, 634 (1982).

5) S. Nagakura, J. Am. Chem. Soc., 80, 520 (1958).

6) H. Yada, J. Tanaka, and S. Nagakura, Bull. Chem. Soc. Jpn., 33, 1660 (1960).

7) S. Fukuzumi and T. Tanaka, Chem. Lett., 1982, 1513.

8) N. Nishimura and T. Motoyama, Bull. Chem. Soc. Jpn., 58, 1013 (1985).

9) N. Nishimura and T. Motoyama, Bull. Chem. Soc. Jpn., 58, 3639 (1985).

10) T. Asano and W. J. le Noble, Chem. Rev., 78, 407 (1978).

11) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, Liebigs Ann. Chem., 661, 1 (1963).

12) H. Tubomura, J. Chem. Phys., 24, 927 (1956).

13) S. Nagakura and M. Gouterman, J. Chem. Phys., 26, 881 (1957).

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