BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 355—358 (1970)

Charge-Transfer Interaction and Chemical Reaction. II. Interaction of *s*-Triaminobenzene with Several Electron Acceptors

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(Received August 5, 1969)

The charge-transfer interaction was studied for systems including *s*-triaminobenzene as electron donor. The formation of 1 : 1 stable outer (π,π) complexes at room temperature was observed for the systems including *s*-trinitrobenzene, trininitrotoluene and tetracyanobenzene as electron acceptors. From the analysis of the observed absorption intensities and peak positions of charge-transfer bands, the equilibrium constants of these complexes were determined and the ionization potential of *s*-triaminobenzene was estimated to be 7.3—7.4 eV. Chloranil was found to form a stable outer (π,π) complex with *s*-triaminobenzene only at low temperature, and to be led to a substitution reaction by raising the temperature. The spectrum of the reaction intermediate, the inner (σ) complex of *s*-triaminobenzene with chloranil, was observed at ~500 mμ. A tentative reaction mechanism was proposed.

Aromatic amines are known to act as electron donors and to form charge-transfer (abbreviated hereafter to CT) complexes with a number of electron acceptors.[1,2] Several workers have reported that some aromatic amines are led to chemical reactions with strong electron acceptors through CT complexes.[3-5] In the preceding paper[6] we gave electronic absorption spectra for solutions containing aniline and chloranil in the mixed solvent of ether-isopropyl alcohol (3 : 1) at various temperatures ranging from 36°K to room temperature. We found that these two molecules form a stable outer (π,π) complex at low temperatures below 200°K but with raising temperature they react with each other yielding 2,5-dichloro-3,6-dianilino-*p*-benzoquinone.

s-Triaminobenzene (abbreviated hereafter to TAB) is known to exhibit a characteristic feature in the fact that protonation occurs more easily on the ring carbon atom than on the nitrogen atom at room temperature and the triaminobenzenium ion is formed.[7] In this connection, we undertook to make a further study on the electron-donating property of TAB, paying special attention to the relation between the CT interaction and chemical reaction. Trinitrotoluene (TNT), *s*-trinitrobenzene (TNB), tetracyanobenzene (TCNB) and chloranil were used as electron acceptors.

Experimental

Materials. TAB was synthesized and purified by the method described previously.[7] Aniline and dimethylaniline were distilled under reduced pressure just before use. *p*-Phenylenediamine was purified by repeated recrystallizations from ethyl ether.

TNT and TNB were recrystallized twice from ethanol and thereafter once from ethyl ether. Chloranil was recrystallized three times from acetone. TCNB[8] was purified by recrystallization from ethanol: mp 258°C in a sealed tube in agreement with the value in literature.[9]

Chloroform was purified by distillation after washing with water. Methylene chloride was dried over calcium chloride and distilled. Ethyl ether was treated with sodium metal and distilled.

Measurements. Electronic absorption spectra were measured with a Cary recording spectrophotometer Model 14M. The spectra at low temperatures were measured by immersing cells in a quartz Dewar vessel containing liquid nitrogen or dry ice-acetone as a refrigerant. Infrared spectra were measured with a Hitachi EPI 2 spectrophotometer, Nujol mulls being used.

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1) A. Zweig, J. E. Lancaster, M. T. Neglia and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 4130 (1964).

2) S. Iwata, J. Tanaka and S. Nagakura, *ibid.*, **88**, 894 (1966).

3) W. Liptay and N. Tamberg, *Z. Elektrochem.*, **66**, 59 (1962).

4) J. W. Eastman, G. Engelsma and M. Calvin, *J. Amer. Chem. Soc.*, **84**, 1339 (1962).

5) Z. Rappoport, *J. Chem. Soc.*, **1963**, 4498.

6) T. Nogami, K. Yoshihara and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969).

7) T. Yamaoka, H. Hosoya and S. Nagakura, *Tetrahedron*, **24**, 6203 (1968).

8) TCNB was prepared in our laboratory by Dr. A. Ishitani who is now at the General Research Institute, Toyo Rayon Co., Ltd.

9) E. A. Lawton and D. D. McRichie, *J. Org. Chem.*, **24**, 26 (1959).

Results and Discussion

Outer (π,π) Complex Formation of TAB with TNT, TNB and TCNB. We measured absorption spectra for various solutions containing TAB as an electron donor and TNT, TNB and TCNB as electron acceptors. Chloroform, ethyl ether and methylene chloride were used as solvents. The results show that TAB interacts with electron acceptors such as TNT, TNB and TCNB to give new absorption bands due to neither electron donor nor acceptor in near ultraviolet and visible regions. Some of the observed bands are shown in Fig. 1. The maximum appears at 440 mμ (in chloroform) and 460 mμ (in ethyl ether) for the TAB-TNT complex; at 460 mμ (in chloroform) and 493 mμ (in ethyl ether) for the TAB-TNB complex; at 420 mμ and 530 mμ for the TAB-TCNB complex in methylene chloride. The peak positions (in eV) of the bands are plotted against those of the CT bands for the hexamethylbenzene (abbreviated hereafter to HMB) complexes with the corresponding acceptors.[2,10] The result given in Fig. 2 shows that the points lie on a straight line. This supports the view that the new bands are interpreted as the CT absorption.

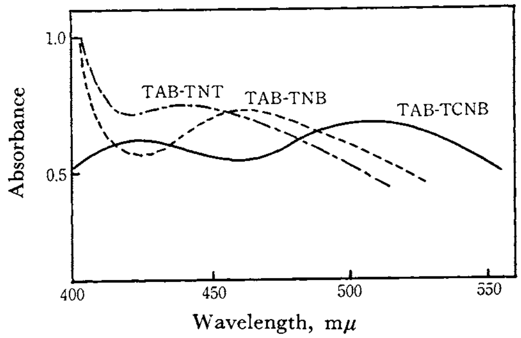

Fig. 1. Spectra of the TAB complexes with TCNB (——) in methylene chloride, and with TNB (- - -) and TNT (— — —) in chloroform.

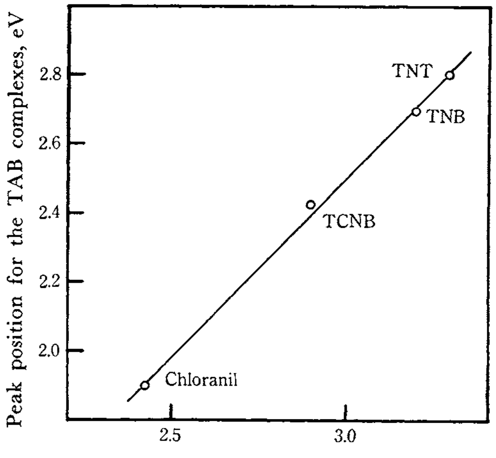

Fig. 2. Plots of the peak positions (in eV) of the new bands observed for the TAB complexes with several electron acceptors in ethyl ether against those of the CT bands for the HMB complexes with corresponding electron acceptors in cyclohexane.

Figure 3 shows that plots of the CT band positions observed for the TNT or TNB complexes with aniline, TAB, dimethylaniline and *p*-phenylenediamine in chloroform against the ionization potentials of the donors except for TAB.[11] From this figure, the electron donating ability of TAB is found to be stronger than that of aniline and weaker than that of dimethylaniline, and its ionization potential can be estimated to be 7.3—7.4 eV.

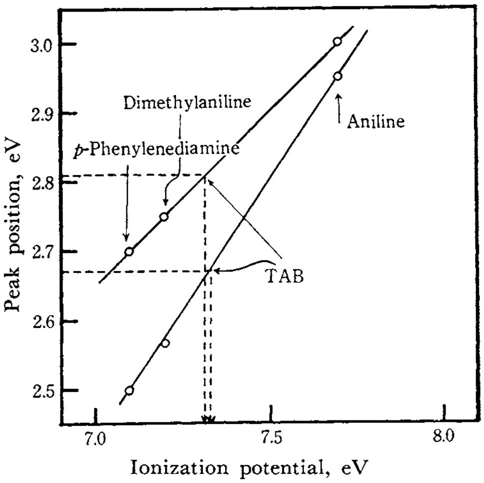

Fig. 3. Plots of the peak positions (in eV) of the CT bands observed for the TNT and TNB complexes against the ionization potentials of aromatic amines as electron donors.

Benesi-Hildebrand plots[12] were carried out for the system containing TAB-TNT and TAB-TNB in chloroform, the well-known straight-line relationship being obtained.[13] This means that 1 : 1 complexes are formed for these systems. The equilibrium constants (K) and the molar extinction coefficients at 25°C were obtained. The results are summarized in Table 1.

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[10] R. Foster and T. J. Thomson, *Trans. Faraday Soc.*, **59**, 296 (1963).

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

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

[13] The concentrations of electron donor C_D and acceptor C_A used for the Benesi-Hildebrand plots are as follows: For TAB-TNT complex, $C_D=2.96\times10^{-3}$ mol/*l*, $C_A=4.04\times10^{-2}$, 2.45×10^{-2}, 1.70×10^{-2} and 1.15×10^{-2} mol/*l*; for TAB-TNB complex, $C_D=2.81\times10^{-4}$ mol/*l*, $C_A=5.56\times10^{-2}$, 2.50×10^{-2}, 1.61×10^{-2} and 1.21×10^{-2} mol/*l*.

Table 1. Equilibrium constant (K) and molar extinction coefficients of CT bands for the TAB-TNT and TAB-TNB system

Complex	$K(\mathrm{mol}^{-1}\,l)$	$\varepsilon_{\max}$
TAB-TNT	15	500
TAB-TNB	20	600

According to Fig. 1, the two CT bands are clearly observed at 420 and 503 mμ for the TCNB-TAB complex in methylene chloride. The frequency difference $\Delta\nu$ between the two peaks is 3920 cm^{-1}. Iwata *et al.*[2] first found that the CT complexes of TCNB with some electron donors show the two CT bands with $\Delta\nu$ values of 5400—6700 cm^{-1}, and these values correspond to the theoretically evaluated energy difference between the two lowest vacant orbitals of TCNB. This means that the two closely located vacant orbitals of the acceptor play an important role in the appearance of the two CT bands for the TCNB complexes. The energy difference (3920 cm^{-1}) is considerably smaller for the TAB-TCNB complex than for the other TCNB complexes. This seems to be related with the fact that the TCNB complex with mesitylene which has the same symmetry as TAB shows a smaller $\Delta\nu$ value than the TCNB complexes with benzene, toluene, durene and hexamethylbenzene.

Outer or Inner Complex Formation and the Reaction of TAB with Chloranil. As mentioned above, TAB forms the stable 1 : 1 outer (π,π) complexes with TNT, TNB and TCNB at room temperature. However, when it interacts with chloranil, the situation seems to be more complex. A blue color formation was observed when TAB was mixed with chloranil in mixed solvent of ether-isopropyl alcohol (3 : 1) at the liquid nitrogen temperature.[14] The color of the solution rapidly turned red immediately after the rigid solution was melted with raising temperature and finally became yellow. However, when the solvent is ethyl ether, the blue color is considerably stable below dry ice-acetone temperature.

The absorption spectra of the TAB-chloranil complex under various conditions are shown in Fig. 4. Curve 1 measured at the liquid nitrogen temperature shows the absorption peak at 660 mμ. This band may be regarded as a CT band. This is supported by the fact that the transition energy of this absorption band fits well into the straight line representing the relation between the CT transition energies of the TAB and hexamethylbenzene complexes with the respective electron acceptors, as is shown in Fig. 2. The blue color of the solution became weaker with rising temperature and this color change was found to be reversible for the temperature change near −170°C.

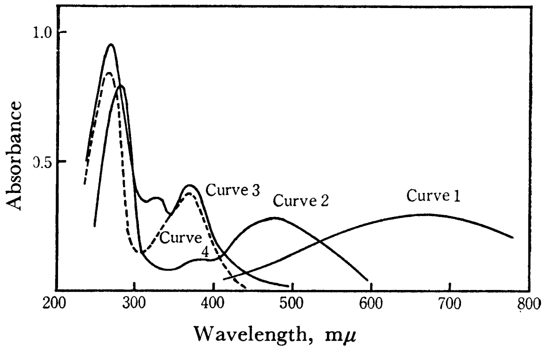

Fig. 4. Time dependence of the spectra for the solution containing 10^{-3} mol/l chloranil and a large excess amount of TAB in 1 : 3 mixed solvent of isopropyl alcohol and ethyl ether. Curve 1, the outer (π, π) complex; curve 2, the inner (σ) complex; curve 3, the adduct of the both components; curve 4, the spectrum of the ring protonated TAB.

As mentioned above, the blue solution containing TAB and chloranil in mixed solvent of ether-isopropyl alcohol turns red in the intermediate state and finally yellow with increasing temperature. The spectral change is shown in Fig. 4. By raising the temperature, curve 1 due to the outer (π,π) complex changes into curve 2 with the absorption peaks at 500 and 370 mμ, and finally we can obtain curve 3, the absorption spectrum of the product which shows the peaks at 220, 272, 320 and 370 mμ.

It is worth noting that curve 2 of Fig. 4 is similar to the absorption spectra observed[15] with the chloranil-methylamine and chloranil-methoxide ion systems which produce the inner complex shown in Figs. 5(a) and 5(b). A similar spectrum was also observed when *N*,*N*-dimethyl-*m*-phenylenediamine, *m*-phenylenediamine or *m*-aminophenol is mixed with chloranil in the etheral solution. We conclude that the spectrum originates from the inner complex[16] shown in Fig. 5(c). This structure was also supported by the molecular orbital calculation.[17]

Let us consider the absorption spectrum given by curve 3 in Fig. 4. The spectrum, except for the

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[14] Actual mixing was carried out by iterating a process of adding only a small amount of the donor solution of room temperature to a large amount of the acceptor solution at liquid nitrogen temperature.

[15] The chloranil-methylamine (in ether and water mixed solvent) and chloranil-methoxide ion (in methanol) systems show the absorption peak at 505 and 475 mμ, respectively. Although these peak wavelengths are somewhat dependent upon the solvent, they, particularly the latter correspond to the 475 mμ peak of curve 2.

[16] Any attempt to isolate the inner complex was unsuccessful, because it easily decomposes on filteration from solutions and on vaporization of solvents.

[17] T. Nogami, K. Yoshihara, T. Yamaoka and S. Nagakura, to be published.

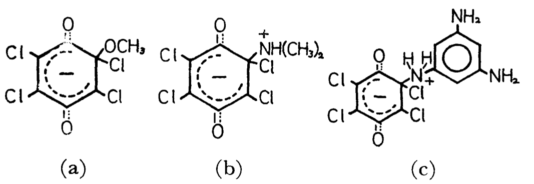


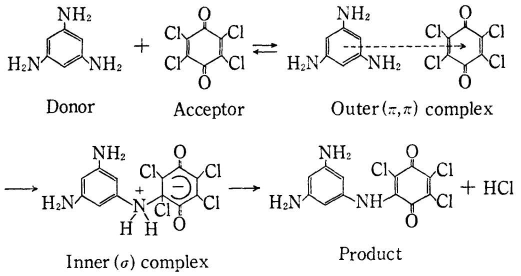
Fig. 5. Structures of intermediate σ complexes.

peak at 320 mμ, agrees well with that of 1,3,5-triaminobenzenium ion.[7,18] The existence of this ion in the system was also demonstrated by the fact that the infrared spectrum measured for the precipitate (in Nujol mulls) produced in the presence of an excess amount of TAB is the same as that of the triaminobenzenium ion.[7]

The peak at 320 mμ seems to be due to another product. This view is supported by the fact that the relative intensity of the 320 mμ band to the bands changes with the conditions.[19] A fairly pure product with the band at 320 mμ is obtained as a precipitate[20] when an excess amount of chloranil is mixed with TAB in acetone. By an analogy with the products of similar reactions of chloranil with aromatic or aliphatic amines,[6,21,22] the precipitate is expected to be 2,5,6-trichloro-3-triaminobenzo-*p*-benzoquinone or/and 2,5-dichloro-3,6-bis(triaminobenzo)*p*-benzoquinone. Elementary analysis shows that the main part of the precipitate in the presence of an excess amount of chloranil is the former.

Found: C, 41.73; H, 4.13; N, 12.9; Cl, 27.37%. Calcd for the former ($C_{12}H_8N_3Cl_3O_2$): C, 43.24; H, 2.40; N, 12.64; Cl, 31.98%. The discrepancy of elementary analysis from the calculated is due to the difficulty in the separation of the triaminobenzenium ion from the precipitate[23] and also to its hygroscopic property. The elementary analysis data can be expalined by taking account of the mixing of small amounts of the triaminobenzenium ion and water. At least it may be concluded that the main product is not 2,5-dichloro-3,6-bis (triaminobenzo)*p*-benzoquinone. The NMR spectrum measured for the deuterated DMSO solution of the precipitate is consistent with the above-mentioned structure of the main product.[24]

From the above-mentioned results on the structures of the reaction intermediates and products, a possible mechanism of the reaction is proposed as follows:



Hydrogen chloride produced in the above reaction attacks TAB to yield the triaminobenzenium ion.[7] For this reason we can observe its absorption spectrum for reaction products.

Increasing the concentration of TAB in solution, we can expect to produce 2,5-dichloro-3,6-bis-(triaminobenzo)*p*-benzoquinone together with 2,5,6-trichloro-3-triaminobenzo-*p*-benzoquinone and the triaminobenzenium ion. Actually, elementary analysis of the product shows that the mixture of the above compounds is precipitated. A similar tendency was also observed by Kumanotani *et al.*[21] for the toluquinone-*n*-butylamine system.

The above-mentioned mechanism with the outer (π,π) and inner (σ) complexes as intermediates was demonstrated to be correct by analyzing the results of the temperature dependence of the decay curve of the inner (σ) complex.[17] The details of this analysis together with a kinetic study on the other systems will be published.

The authors wish to express their gratitude to Professor Takahiro Tsunoda, the University of Chiba, for his continuous encouragement throughout the course of this research. They are also greatly indebted to Dr. Keitaro Yoshihara and Mr. Takashi Nogami for their helpful discussion.

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18) H. Köhler and G. Scheibe, *Z. Anorg. Allg. Chem.*, **385**, 221 (1956).

19) For example, the 320 mμ band becomes relatively stronger for the product obtained from the dilute solution containing a great excess amount of chloranil.

20) The precipitate exhibits no infrared band due to the 1,3,5-triaminobenzenium ion. However, it is shown to include a small amount of the ion from visible and ultraviolet absorption measurement.

21) J. Kumanotani, F. Kagawa, A. Hikosaka and K. Sugita, This Bulletin, **41**, 2118 (1968).

22) D. Buckley, H. B. Henbest and P. Slade, *J. Chem. Soc.*, **1957**, 4891.

23) We tried to separate each product by chromatography and other methods, but we were not successful mainly because of the very small solubility of the precipitate.

24) The NMR spectrum of the precipitate in deuterated DMSO solution shows three peaks at $\tau=6.40$, 4.30 and 2.80 which are assigned to the proton signals of NH_2, ring and NH from their τ values and intensities. For the purpose of comparison, the NMR spectra of triaminobenzene and diphenylamine were also measured with the results: $\tau=7.20$ (NH_2 proton), 4.60 (ring proton) for triaminobenzene; $\tau=1.89$ (NH proton) for diphenylamine.