Charge-Transfer Interaction between *N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine and Chloranil

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As an extension of a series of studies[1] of charge-transfer (CT) interactions between aromatic amines and chloranil, we measured temperature and concentration dependencies of an electronic absorption spectrum for a system including *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and chloranil in an ethyl ether-isopropyl alcohol (3 : 1) mixed solvent.

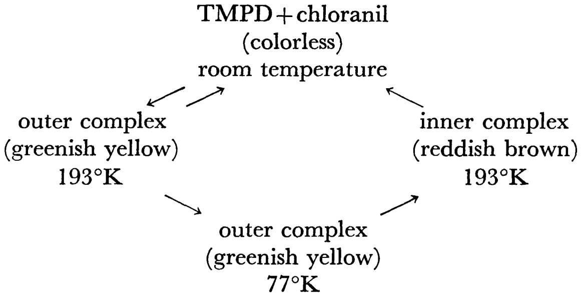
The system showed spectra due to two different kinds of complexes. One is greenish yellow and exhibits an absorption peak at 830 mμ. This band was identified by Foster and Thomson[2] as the CT band of the outer complex. The other is reddish brown and has absorption peaks at 1100, 635, 520, and 434 mμ. The 1100 mμ band corresponds to a reverse CT band ($D \cdot A \leftarrow D^+A^-$) of the inner (ion-pair or ionic EDA) complex observed by Sato *et al.*[3] for the solid TMPD-chloranil. We studied the behaviors of these two specimens in the solution by measuring their absorption spectra at room temperature, 193°K and 77°K. In Table 1, the observed results, A, B, C, D, and E denote the following phenomena. A: Immediately after mixing the TMPD and chloranil solutions at room temperature, the outer complex is formed and converted gradually into the inner complex. B: Only the outer complex is formed at room temperature, and the inner-complex formation starts by lowering the temperature of the solution to 193°K. C: Only the outer complex is formed in the temperature range from room temperature to 193°K, and the inner-complex formation starts at 77°K. D: The component molecules which are almost completely free at room temperature start to form the outer complex at 193°K. This process is reversible. By raising the solution temperature to 193°K after once having lowered it to 77°K, the inner complex is formed. By raising the temperature further, the solution returns to the initial stage at room temperature. E: Only the outer complex is formed in the range of 193°K to 77°K, and the inner complex is not formed.

TABLE 1. TEMPERATURE AND CONCENTRATION DEPENDENCIES OF THE CT COMPLEXES BETWEEN TMPD AND CHLORANIL

[D][a]	[A][a]		
	20	5	1.25
160	A	B	C
80			
40	B		
20			
10		C	
5	C		
2.5			D
2			
1.75	D	D	E
1.25			
1	E	E	
0.75			

a) [D] and [A] are the concentrations (in the unit of 10^{-4} mol/*l*) of TMPD and chloranil, respectively.

The present results of the outer-complex formation are reasonable and can be explained by the equilibrium-shift toward the outer-complex formation caused by the lowering of temperature. The results concerning the inner complex, though rather complicated, suggest that its formation can not occur unless the outer-complex concentration exceeds some limited values. This seems to show that the inner-complex formation needs environmental cooperation; in particular, that there must be a clustering of donor-acceptor pairs before the inner-complex formation begins.[4] In this connection, phenomenon D is particularly interesting as showing the following color cycle with temperature:



The colorless solution at room temperature turns greenish yellow at 193°K and the color becomes deeper by decreasing the temperature to 77°K. The solution changes from greenish yellow to reddish brown by raising the temperature from 77°K to 193°K.[5] By raising further the temperature, the solution returns to the initial colorless state. The color cycle occurs regardless of the lowering and raising rates of temperature and can be repeated many times. Although the mechanism of the inner-complex formation in this cycle is not clear at the present stage, the phenomenon seems to support the opinion that the outer complex is a precursor to the inner-complex formation in the reaction path.

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[1] T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969); T. Yamaoka and S. Nagakura, This Bulletin, **43**, 355 (1970); T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, *ibid.*, to be published.

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

[3] Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, This Bulletin, **43**, 2370 (1970).

[4] Mulliken presented a similar view for the formation of $NH_4^+Cl^-$ crystals from NH_3 and HCl gases (R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952)).

[5] This process is irreversible.