Charge-transfer Interaction and Chemical Reaction. IV. Reactions of *para*-Substituted Derivatives of Aniline with Chloranil

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(Received July 20, 1971)

Interactions of chloranil with *p*-phenylenediamine, *N,N*-dimethyl-*p*-phenylenediamine, and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine were studied by measuring visible and ultraviolet absorption spectra at various temperatures between 77°K and 300°K. In an ether-isopropyl alcohol (3:1) mixed solvent, the *p*-phenylenediamine- and *N,N*-dimethyl-*p*-phenylenediamine-chloranil systems were led to the substitution reaction through the outer complex and the ionic species as reaction intermediates. In ethyl ether, the *p*-phenylenediamine- and *N,N*-dimethyl-*p*-phenylenediamine-chloranil systems were found to yield the inner complex and the substituted species through the outer complex, respectively. In the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine-chloranil system, the inner complex was found to be formed *via* a clustering of the outer complexes.

The interactions between aromatic amines and chloranil were found to be classified into the following three types: (a) the charge-transfer (outer or inner) complex is formed between an electron donor and an acceptor and no further reaction proceeds; (b) the substitution reaction occurs through the outer and inner complexes; (c) the substitution reaction occurs through the outer complex and ionic species. The difference in the reactivities between *meta*-substituted derivatives of aniline and *ortho*- and *para*-substituted ones was explained by taking the π-electron density on the amino group into account.

In previous papers of this series,[1] the reactions of several aromatic amines with chloranil were studied from the viewpoint of charge-transfer interaction. Detailed studies were made of the reactions of chloranil with aniline,[1a] 1,3,5-triaminobenzene,[1b] and *m*-phenylenediamine.[1d] In these three systems, the substitution reactions were found to occur through the outer and inner complexes as the reaction intermediates. A detailed kinetic study was made of the third case by measuring the formation and decay curves of the inner complexes, and the potential energy curves of the reactions were determined experimentally. Substitution reactions of a similar mechanism were found to occur for the systems including chloranil and several *meta*-substituted derivatives of aniline (*m*-anisidine, *m*-aminophenol, *N,N*-dimethyl-*m*-phenylenediamine, *N,N,N',N'*-tetramethyl-*m*-phenylenediamine, and 1-methyl-2,4,6-triaminobenzene).

On the other hand, another type of reactions were found for systems containing *ortho*- or *para*-substituted derivatives of aniline and chloranil. The main purposes of the present study are to clarify the mechanism for the interaction of chloranil with *p*-substituted anilines and to obtain information on the effect of the position of the substituted group upon the reaction mechanism. For these purposes, we took *p*-phenylenediamine (PD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD), and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) as electron donors. Furthermore, the classification of the reactions between chloranil and various aromatic amines is described on the basis of the π-electron density on the amino group by comparing the *meta*-substituted derivatives of aniline with *ortho*- and *para*-substituted ones.

Experimental

Materials. PD, DMPD, and TMPD were purified by vacuum sublimation. Chloranil was purified by repeated recrystallizations from acetone.

Measurements. A Cary recording spectrophotometer model 14 M was used for the measurements of electronic absorption spectra, a quartz cell with a 1-cm light path length being used. The donor and acceptor solutions, which were separately prepared, were mixed with each other immediately before the absorption measurements at low temperatures. For the measurements at low temperatures, a sample cell was immersed in a quartz dewar vessel designed for the spectroscopic measurements and was cooled with cold nitrogen gas. The temperature was regulated by nitrogen-flow velocity.

Results and Discussion

Reaction of PD with Chloranil. We studied the interaction of chloranil with PD, DMPD, and TMPD using ethyl ether and ether-isopropyl alcohol (3: 1) as solvents. First of all, let us describe the results for the PD-chloranil system in ethyl ether.

After mixing the ethyl ether solutions of PD and chloranil at a low temperature (the concentrations of PD and chloranil in the final solution were 6.7×10^{-4}M and 3.3×10^{-4}M, respectively), the change in the absorption spectra was measured. The 785 and 390 nm bands assigned to the outer complex[2] appear at first and decrease in intensity with increasing temperature. After the solution was kept at room temperature for a few hours, a blue species gradually precipitated. The absorption spectra of the precipitate, which was mea-

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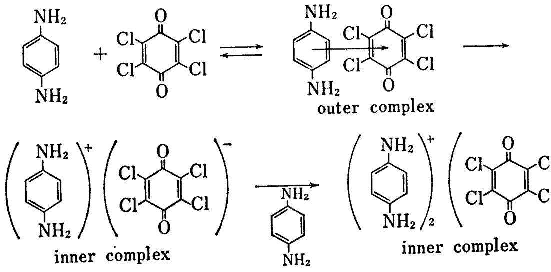
[1] (a) T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969); (b) T. Yamaoka and S. Nagakura, This Bulletin, **43**, 355 (1970); (c) T. Nogami, K. Yoshihara, and S. Nagakura, *ibid.*, **44**, 295 (1971); (d) T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, *ibid.*, **44**, 380 (1971).

[2] This assignment was made from the relation between the peak position of the charge-transfer absorptions observed with the chloranil complexes and the ionization potentials of several electron donors.

sured by coating the powdered sample on a glass plate by a stainless steel spatula,[3] were found to consist of the absorption bands of the 2: 1 (PD: chloranil) complex (380, 590, and 670 nm) plus the charge-transfer absorption band of the 1: 1 complex (850 nm).[4] The elemental analysis data of the precipitate show that it is a mixture of about 90% of the 2: 1 complex and about 10% of the 1: 1 complex. These two complexes show an ESR signal.[4] This indicates the formation of ion pair type complexes which may be denoted by inner complexes. From the above-mentioned experimental facts, the reaction mechanism of the system under consideration may be represented as follows:



Next, let us turn to the PD-chloranil system in an ether-isopropyl alcohol (3: 1) mixed solvent. After mixing the solutions of PD and chloranil in the mixed solvent (the concentrations of PD and chloranil in the final solution were 6.7×10⁻⁴M and 3.3×10⁻⁴M, respectively) at 193°K, the temperature dependence of the absorption spectrum was measured; the results are shown in Fig. 1. At first, the absorption bands of the outer complex appear; then they decrease in intensity with the increasing temperature. With the decrease in the bands due to the outer complex, new bands due to the PD cation monomer (500 and 465 nm) and dimer (605 nm)[5] appear with the isosbestic points at 430 and 640 nm. This fact shows that the outer complex directly converts into the cation monomer and dimer.

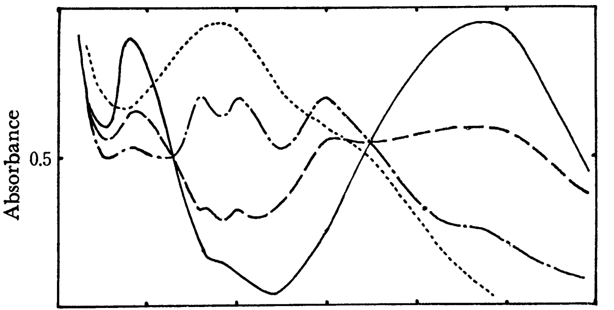


Fig. 1. The absorption spectra of the PD—chloranil system in an ethyl ether-isopropyl alcohol (3 : 1) mixed solvent; [PD]=6.7×10⁻⁴M, [chloranil]=3.3×10⁻⁴M.

—— The absorption spectrum measured immediately after mixing at 193°K; the spectrum of the outer complex.

- - - The absorption spectra measured at 225°K; the spectra of the outer complex and of the PD cation monomer and dimer.

- • - The absorption spectra measured at 235°K; the spectra of the PD cation monomer and dimer.

······ The absorption spectrum measured at room temperature; the spectrum of the final reaction product.

The ionic specimens do not cause succeeding reactions at temperatures lower than 230°K. When the solution is recooled from 230°K to 193°K, the absorption bands of the outer complex and cation dimer always increase in intensity and those of the cation monomer disappear. However, the outer complex bands do not completely recover the initial absorbance at 193°K.

The absorption bands due to the chloranil anion (426 and 455 nm)[6] can not be detected, probably because the concentration of the chloranil anion is rather low and its absorption band may be covered by those of the outer complex, the PD cation monomer, and a final reaction product.

By raising the temperatures of the solution to room temperature, the absorption bands due to the outer complex and to the PD cation monomer and dimer disappear in a few minutes; thereafter, those due to the final reaction product (460 and 630 nm) gradually increase the intensity for a few hours. The elemental analysis of the reaction product corresponds to $C_{18}H_{14}Cl_2N_4O_2$[7] and indicates that it is 2,5-dichloro-3,6-di-*p*-aminoanilino-*p*-benzoquinone.

In order to clarify whether the PD cation monomer and dimer exist as reaction intermediates in the main reaction path or only in the side reaction, the time dependences of the absorption spectra of the PD cation and final reaction product were measured in the temperature range from −15°C to 0°C[8]; the result is shown in Fig. 2. The absorption band of the PD cation at 450—500 nm is covered by that of the final reaction product; therefore, the vibrational structure of the former band is smeared out with the latter band as the reaction proceeds. From Fig. 2, we can obtain[9]

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[3] T. Sakata and S. Nagakura, This Bulletin, **42**, 1497 (1969).

[4] Dr. Sakata in our laboratory obtained the 2:1 complex (PD: chloranil) by adding PD to the 1: 1 CT complex in ethanol. The 1:1 complex was prepared by mixing the benzene solutions of PD and chloranil.

[5] K. Kimura, H. Yamada, and H. Tsubomura, *J. Chem. Phys.*, **48**, 440 (1968).

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

[7] The PD—chloranil system in ethyl ether-isopropyl alcohol (3:1) mixed solvent. Found: C, 54.16; H, 4.21; Cl, 17.58; N, 15.81%. Calcd for $C_{18}H_{14}Cl_2N_4O_2$: C, 55.52; H, 3.59; Cl, 18.25; N, 14.39%. The DMPD—chloranil system in ethyl ether. Found: C, 58.43; H, 5.00; Cl, 16.28; N, 12.07%. Calcd for $C_{22}H_{22}Cl_2N_4O_2$: C, 59.32; H, 4.94; Cl, 15.95; N, 12.58%. The DMPD—chloranil system in ethyl ether-isopropyl alcohol (3:1) mixed solvent. Found: C, 59.24; H, 4.88; Cl, 15.56; N, 12.55%. Calcd for $C_{22}H_{22}Cl_2N_4O_2$: C, 59.32; H, 4.94; Cl, 15.95; N, 12.58%. The agreement between the found and the calculated is not good for the PD—chlornail system in the mixed solvent. The discrepancy may be due to the difficulty in removing the 1:1 substitution product and other impurities and also to their hygroscopic property. We tried to separate each product by chromatography and other methods, but we did not succeed mainly because of very small solubility of the precipitate.

[8] Because of the difficulty of keeping the temperature constant, we measured the absorption spectra without controlling the temperature.

[9] The absorption intensities at 630 and 500 nm were measured at some time intervals determined by the wavelength scanning speed. Since the reaction is rather fast, we can not ignore the absorption intensity change which occurs during the intervals. Therefore, in the analysis of the experimental results, we made a suitable correction for this change.

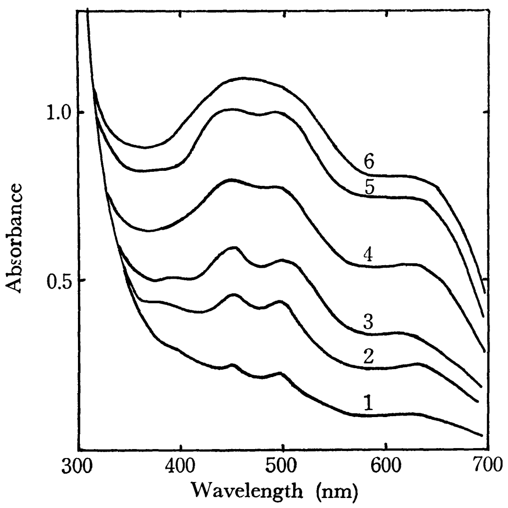

Fig. 2. The time dependence of the absorption spectrum of the PD—chloranil system in an ether-isopropyl alcohol (3: 1) mixed solvent; [PD]$=5.0\times10^{-4}$M, [chloranil]$=2.5\times10^{-4}$M. Curves 1, 2, 3, 4, 5, and 6 are, respectively, the spectrum measured at 3, 7, 11, 19, 40, and 73 min after the mixing of the donor and acceptor solutions at −15°C. The temperature increased gradually from −15 to 0°C during the measurements.

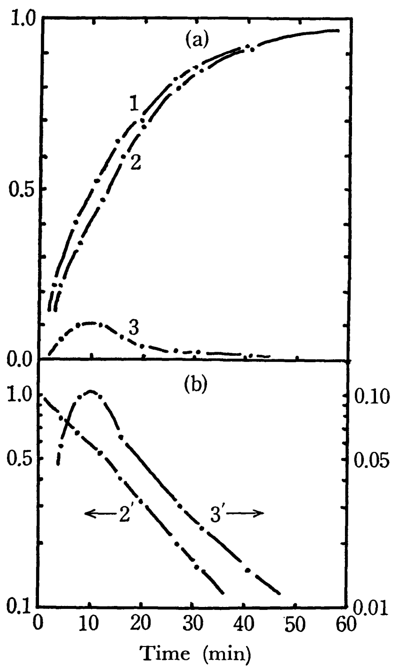

Fig. 3. The time dependence of the absorption intensities of the PD cation and the reaction product derived from the curves shown in Fig. 2. (a); the ordinate is $I_{500}/I_{500}^{\max}$, $I_{630}/I_{630}^{\max}$, and $I_{500}/I_{500}^{\max}-I_{630}/I_{630}^{\max}$ for curves 1, 2, and 3, respectively: (b); the ordinate is $(I_{630}^{\max}-I_{630})/I_{630}^{\max}$ and $I_{500}/I_{500}^{\max}-I_{630}/I_{630}^{\max}$ for curves 2′ and 3′, respectively. The left- and right-hand side ordinates are concerned with curves 2′ and 3′, respectively.

the time dependences of the absorption intensities at 500 and 630 nm ($I_{500}/I_{500}^{\max}$ and $I_{630}/I_{630}^{\max}$, respectively), as shown in Fig. 3[10]. Here, I_{500} and I_{630} denote the absorption intensities at 500 and 630 nm, respectively; the superscript "max" means that the corresponding quantity is the value at the final stage of the reaction.

I_{500} is concerned with both the PD cation and the reaction product, but I_{630} with only the reaction product.[10] Therefore, we can obtain an information about the time dependence of the absorption intensity of the PD cation by calculating the $I_{500}/I_{500}^{\max}-I_{630}/I_{630}^{\max}$ value at each time. Curves 1, 2, and 3 in Fig. 3(a) represent the time dependences of the values, $I_{500}/I_{500}^{\max}$, $I_{630}/I_{630}^{\max}$, and $I_{500}/I_{500}^{\max}-I_{630}/I_{630}^{\max}$, respectively. In Fig. 3(b), the time dependence of $[I_{630}^{\max}-I_{630}]/I_{630}^{\max}$ is compared with that of $[I_{500}/I_{500}^{\max}-I_{630}/I_{630}^{\max}]$. The two curves in Fig. 3(b) are almost parallel to each other after 15 min. This means that the decreasing rate of the PD cation is almost equal to the increasing rate of the reaction product. Therefore, the PD cation undoubtedly takes part in the main reaction path as an intermediate and plays an important role in the reaction of PD with chloranil in an ether-isopropyl alcohol (3: 1) mixed solvent. Although the details of the mechanism are not clear, it seems probable that the reaction proceeds through the interaction between the chloranil anion and the PD cation (or its dimer).

Reaction of DMPD with Chloranil. The ether solution containing DMPD and chloranil shows absorption bands due to the outer complex at 815 and 390 nm[2] at 193°K. With the increasing temperature, the intensities of these bands decrease and absorption bands due to a final reaction product which appear at 460 and 670 nm increase in intensity. The elemental analysis of the reaction product corresponds to $C_{22}H_{22}Cl_2N_4O_2$,[7] indicating that it is 2,5-dichloro-3,6-di-*p*-dimethylaminoanilino-*p*-benzoquinone. The infrared absorption measurements also support this identification.[11] No reaction intermediate could be detected between the outer complex and the final reaction product. Two reaction mechanisms are conceivable in this solvent, *i.e.*, a substitution reaction through the outer and inner (σ) complexes and one through the outer complex and ionic species. If the former is the case, the reaction mechanism of the system under consideration is phenomenologically similar to that of the aniline-chloranil system[1a] in the sense that we can not detect spectrophotometrically the inner complex through which the reaction may be expected to proceed. From only the above experimental facts, we can not conclude which of these two reactions actually occurs.

In an ether-isopropyl alcohol (3: 1) mixed solvent, the reaction of DMPD with chloranil is similar to that of the PD-chloranil system in the same solvent because, in both systems, the substitution reaction occurs through the outer complex and such ionic species as the donor cation, which exists in an equilibrium between the monomer and the dimer. Figure 4 shows the change in the absorption spectrum with the progress of the reaction of DMPD with chloranil. The cation dimer and monomer have absorption maxima at 670 nm and at 523 and 570 nm,[5] respectively. The final reaction product which has absorption bands at 460 and 670 nm was identified as 2,5-dichloro-3,6-di-*p*-dimethylaminoanilino-*p*-benzoquinone by an elemental analysis.[7] The absorption bands due to ionic species

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[10] The temperature is high enough to disregard the absorption due to the PD cation dimer at 605 nm.

[11] One band of the N–H stretching mode was observed at 3180 cm^{-1}.

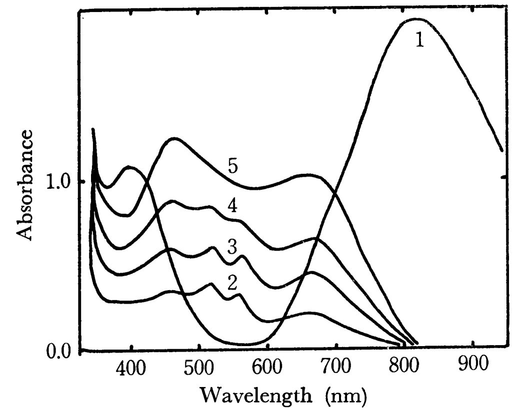

Fig. 4. The absorption spectra of the DMPD-chloranil system in an ether-isopropyl alcohol (3: 1) mixed solvent; [DMPD] $=5.0\times10^{-4}$M, [chloranil] $=2.5\times10^{-4}$M. Curve 1, is the absorption spectrum measured at 198°K; the spectrum of the outer complex. Curves 2, 3, 4, and 5 are the spectra measured at 17, 28, 45, and 129 min after the mixing at 253°K. During the measurements, the temperature increased from 253 to 273°K.

disappear almost completely at room temperature a few minutes after the mixing and those due to the final reaction product gradually increase. No reaction intermediate was found between the ionic species and the final reaction product.

Interaction of TMPD with Chloranil. The temperature and concentration dependencies of this system were investigated by studying the electronic absorption spectra in an ethyl ether-isopropyl alcohol (3: 1) mixed solvent. The system showed two different kinds of complexes. One of them is greenish yellow and exhibits an absorption peak at 830 nm. This band was identified by Foster and Thomson as the CT band of the outer complex.⁶⁾ The other is reddish-brown and has absorption peaks at 1100, 635, 520, and 434 nm. The 1100 nm 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, Kinoshita, Sano, and Akamatu for the solid TMPD-chloranil complex.¹²⁾

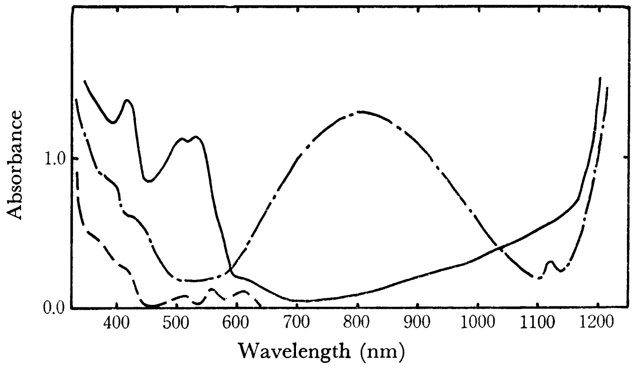

Fig. 5. The absorption spectra of the TMPD—chloranil system in an ethyl ether-isopropyl alcohol (3: 1) mixed solvent; [TMPD] $=1.25\times10^{-4}$M, [chloranil] $=1.0\times10^{-3}$M.

- - - The absorption spectrum measured at room temperature; the spectrum of TMPD cation superposed on the spectra of the component molecules.

- • - The absorption spectrum measured at 77°K; the spectrum of the outer complex.

—— The absorption spectrum measured at 193°K after once having lowered to 77°K; the spectrum of the inner complex. The 1100 nm band is very broad and appears as a shoulder of a strong band due to solvent molecules.

TABLE 1. CONCENTRATION AND TEMPERATURE DEPENDENCIES OF THE CT COMPLEX FORMATIONS BETWEEN TMPD AND CHLORANIL IN AN ETHYL ETHER-ISOPROPYL ALCOHOL (3:1) MIXED SOLVENT

[D]ᵇ⁾ \ [A]ᵃ⁾	2	1	1/2	1/4	7/40	1/40
16	A	A	B	C	C	C
8		B				
2	B					
1		C	C			
1/2	C					
9/40					D	D
1/5						
7/40	D	D	D	D		E
3/20						
1/8				E	E	
1/10	E	E	E			

a) [A] denotes the concentration of chloranil in the unit of 10^{-3} M.

b) [D] denotes the concentration of TMPD in the unit of 10^{-3} M.

We studied the behaviors of these two specimens in solutions of various concentrations of the components by measuring their absorption spectra at room temperature, 193°K, and 77°K; as an example, the temperature dependence of the spectrum observed with the solution consisting of 1.25×10^{-4}M TMPD and 1.0×10^{-3}M chloranil is shown in Fig. 5.¹³⁾ The results obtained for the solutions containing various concentrations of the components are classified and tabulated in Table 1. In this table, 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 is gradually converted into the inner complex which precipitates as a reddish-brown crystal. At this stage, the outer and inner complexes coexist in the solution. B: The solution is green at room temperature because of the outer complex formation. The inner-complex formation starts by lowering the temperature of the solution to 193°K and the solution turns reddish-brown without a precipitate. The solution becomes green again by raising its temperature. 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 pro-

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

13) The concentrations of D and A in this solution correspond to class D in the classification of Table 1.

cess is reversible. By raising the solution temperature to 193°K after having once 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 from 193°K to 77°K; the inner complex is not formed.

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 the 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 value. 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.[14] In this connection, phenomenon D is particularly interesting as showing the following color cycle with the temperature:

TMPD + chloranil
(colorless)
room temperature
↙↗ ↖
outer complex (greenish-yellow) 193°K inner complex (reddish-brown) 193°K
↘ ↗
outer complex
(greenish-yellow)
77°K

The colorless solution at room temperature turns greenish-yellow at 193°K; 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.[15] 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 the temperature and can be repeated many times.

In order to investigate the process from the outer complex to the inner complex, we measured the change in the scattering light intensity with the time, using a He–Ne gas laser as the light source. After keeping a cell containing the solution of TMPD and chloranil in the mixed solvent (the concentrations of TMPD and chloranil were 1.25×10^{-4}M and 5.0×10^{-4}M, respectively, corresponding to D in Table 1) to 77°K, we set it in a dewar vessel designed for the optical measurement and started the measurement of the scattering light intensity as soon as possible.

The inner complex is formed as the temperature of the solution is raised by acetone of room temperature surrounding the cell in the dewar vessel; thereafter, it dissociates into its component molecules. Corresponding to the change in the inner-complex concentration with the time, the scattering light intensity changes, as is shown in Fig. 6. Briefly speaking, the time-change of the scattering light intensity shown in this figure is parallel to that of the concentration of the inner complex. This seems to support the view that the clustering of the outer complexes is related to the formation of the inner complex.[16] As pointed out by Mulliken,[17] a potential barrier between the outer and inner complexes may be expected to decrease with the increase in the polarity of the environment caused by the clustering.

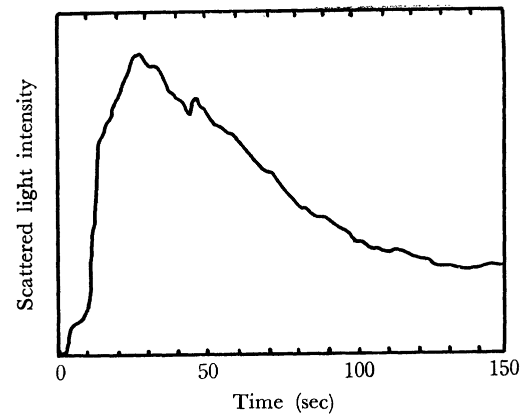

Fig. 6. The time dependence of the scattered light intensity measured for the solution containing TMPD and chloranil in an ethyl ether-isopropyl alcohol (3: 1) mixed solvent, $[\mathrm{TMPD}]=1.25\times10^{-4}$M, $[\mathrm{chloranil}]=5.0\times10^{-4}$M. With the rapid temperature rising from 77°K to room temperature, the scattered light intensity increases and decreases corresponding to the formation and decay of the inner complex, respectively.

A similar phenomenon was observed when we used ethyl ether as the solvent instead of an ethyl ether-isopropyl alcohol (3: 1) mixed solvent. Furthermore, both solvents are not enough polar to dissociate the inner complex between TMPD and chloranil into the ions, although the system is known to ionize in such a polar solvent as a chloroform-ethanol (1: 1) mixed solvent.[18]

Classification of Interactions of Aromatic Amines with Chloranil. On the basis of the results described in previous papers[1a–1d] and in the present paper, the interactions of various aromatic amines with chloranil in ethyl ether and in an ethyl ether-isopropyl alcohol (3: 1) mixed solvent can be classified as in Table 2. In this classification, the interactions are briefly divided into three classes, (a), (b), and (c), and each of the first two is further divided into two subclasses.

(a) The charge-transfer complex is stable and no further reaction proceeds. This class is divided further into two subclasses.

(a1) Only the outer complex is formed.

$$\mathrm{D} + \mathrm{A} \rightleftarrows \mathrm{D}\cdot\mathrm{A}$$

(An example of D in this subclass is diphenylamine)

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

[15] This process is irreversible.

[16] The details of the light-scattering experiment will be published in a forthcoming paper.

[17] R.S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[18] I. Isenberg and S. L. Baird, *J. Amer. Chem. Soc.*, **84**, 3803 (1962).

Table 2. IONIZATION POTENTIALS OF AROMATIC AMINES, MAXIMUM WAVELENGTHS OF CT ABSORPTIONS OF THEIR COMPLEXES WITH CHLORANIL, AND THEIR CHEMICAL REACTIVITIES WITH CHLORANIL

Amine	I_p[a] (eV)	λ_{CT} (nm)	Classification of reaction
Diphenylamine	7.1	655	a1
Aniline	7.69[b]	556	b1
o-Toluidine	7.7	555	b1
m-Toluidine	7.50[b]	555	b1
p-Toluidine	7.4	600	b1
o-Anisidine	7.6	568	—
m-Anisidine	7.6	567	b2
p-Anisidine	7.3	616	—
o-Aminophenol	7.6	567	—
m-Aminophenol	7.5	580	b2
p-Aminophenol	7.5	578	—
o-PD[c]	6.9	710	c
m-PD	7.0	680	b2
p-PD	6.8	785	a2, c[d]
1,3,5-Triaminobenzene	7.1	660	b2
1-Methyl-2,4,6-triaminobenzene	7.0	680	b2
N,*N*-dimethylaniline[e]	7.2	650	c
N,*N*-dimethyl-*m*-phenylenediamine	7.0	680	b2
DMPD	6.5	815	b1 or c, c[f]
N,*N*,*N'*,*N'*-tetramethyl-*m*-phenylenediamine	—	g)	b2
TMPD	6.5	830	a2

a) Estimated from the absorption peak positions of the corresponding outer complexes with chloranil except for aniline and *m*-toluidine.

b) F. I. Vilesov, *Soviet Phys. Usp.*, **6**, 888 (1964).

c) In the *o*-phenylenediamine–chloranil system, the outer complex was found to produce some ionic species as reaction intermediates, although the ionic species and the final reaction product are not yet identified.

d) The a2 and c were found in ethyl ether and in an ethyl ether-isopropyl alcohol (3:1) mixed solvent, respectively.

e) In *N*,*N*-dimethylaniline–chloranil system, the outer complex ionizes into the *N*,*N*-dimethylaniline cation and the chloranil anion, and thereafter, the cation produces crystal violet as a final product in acetonitrile. J. W. Eastman, G. Engelsma, and M. Calvin, *J. Amer. Chem. Soc.*, **84**, 1339 (1962). Similar reaction processes were found by us in ethyl ether or in an ethyl ether-isopropyl alcohol (3:1) mixed solvent.

f) The b1 or c and c were found in ethyl ether and in an ethyl ether-isopropyl alcohol (3:1) mixed solvent, respectively.

g) The absorption spectrum of the outer complex has not been measured.

(a2) Both outer and inner complexes are formed.

$$D + A \rightleftarrows D\cdot A \longrightarrow D^+A^-$$

(An example of D in this subclass is TMPD)

(b) The substitution reaction proceeds through the outer and inner complexes.

$$D + A \rightleftarrows D\cdot A \longrightarrow D^+A^- \cdots \longrightarrow P$$

This class is also phenomenologically divided into two subclasses.

(b1) The inner complex is too unstable to be observed by electronic absorption measurements. Aniline is an example of D in this subclass.[1a]

(b2) The inner complex can be observed by electronic absorption measurements. *m*-Phenylenediamine is an example of D in this subclass.[1d]

(c) The reaction proceeds through the outer complex and the ionic species as the reaction intermediates.

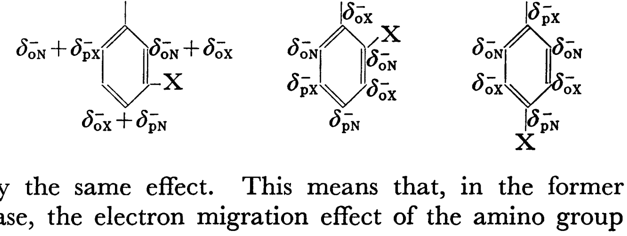
$$D + A \rightleftarrows D\cdot A \longrightarrow D^+ \text{ (or } D_2{}^{2+}) + A^- \cdots \longrightarrow P$$

(An example of D in this class is PD in an ethyl ether-isopropyl alcohol (3:1) mixed solvent)[19]

In the above classification, D, A, D·A, D^+A^-, D^+, $D_2{}^{2+}$, A^-, and P represent aromatic amine, chloranil, the outer complex, the inner complex, the aromatic amine cation, its dimer, the chloranil anion, and the final product, respectively.

Stability of the Inner Complex. In a previous paper[1d], we pointed out that there exists a parallel relationship between the electron-donating abilities of the *meta*-substituent groups in *meta*-derivatives of aniline and the stabilities of their inner complexes with chloranil. For instance, the inner complex formed between *m*-phenylenediamine and chloranil exists about two hours at room temperature, while the complex with *m*-anisidine lasts only a few seconds. The inner complex can not be observed for the system including chloranil and toluidine which has a weaker electron-donating substituent at the *meta*-position than does *m*-anisidine. This fact was explained[1d] on the basis of the reasonable expectation that the nonbonding electron density on the nitrogen atom of the amino group increases with the electron-donating ability of the *meta*-substituent. From the same point of view, we shall consider the difference in stability between the inner complexes of chloranil with *meta*-substituted anilines and *ortho*- or *para*-substituted anilines.

From Table 2 we can deduce the general tendency that aniline derivatives having the electron-donating substituent(s) at the *meta*-position can form such stable inner complexes as can be detected spectroscopically as intermediates in the substitution reactions. As is clearly seen from the following figure in which the electron-density increments on the carbon atoms at the *ortho*- and *para*-positions of the substituent group (s= X or NH_2) are designated by δ^-_{os} and δ^-_{ps}, respectively, in the case of the *meta*-substituted derivatives of aniline, both the amino group and the *meta*-substituent group act to increase the π-electron densities on the three carbon atoms (*ortho* and *para* carbon atoms) by their electron migration effect, while in the case of *ortho*- and *para*-substituted derivatives of aniline, the π-electron densities on all six carbon atoms increase almost equally



by the same effect. This means that, in the former case, the electron migration effect of the amino group

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[19] The contribution of A^- to this type of reaction is not certain.

is hindered to a greater extent by that of the *meta*-substituent group; therefore, the nonbonding electron density on the amino group is greater than in the latter case. Since the electron-donating ability of aromatic amines in the case of the inner-complex formation may be considered to increase with an increase in the nonbonding electron density on the nitrogen atom of the amino group, the *meta*-substituted derivatives of aniline may be expected to form more stable inner complexes with chloranil than do the *ortho*- and *para*-substituted derivatives.

The ionization potentials (I_p's) of the aromatic amines used as electron donors and the observed peak positions, (λ_{CT}), of the CT bands of the corresponding outer complexes with chloranil are also tabulated in Table 2. Neither the I_p's nor the λ_{CT}'s exhibit any tendency characteristic of the aniline derivatives with an electron-donating substituent(s) at the *meta*-position of the amino group. This may be reasonable, because they are mainly connected with the donor ability of the π-electrons on the benzene ring, while the inner-complex formation is connected with that of the nonbonding electrons of the amino group.

We should like to express our sincere gratitude to Dr. Tomihiko Ohsawa, The Institute of Physical and Chemical Research and Dr. Nobuharu Takai, The Institute of Industrial Science, The University of Tokyo, for their help in the purification of the reaction products.