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Charge Transfer Interaction and Chemical Reaction. III. Reactions of *m*-Phenylenediamine and Related Compounds with Chloranil

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The interactions of chloranil with several aromatic amines were studied by measuring visible and ultraviolet absorption spectra at various temperatures between 70°K and 300°K, *m*-aminophenol, *m*-phenylenediamine, *N,N*-dimethyl-*m*-phenylenediamine, 1,3,5-triaminobenzene, and 1-methyl-2,4,6-triaminobenzene being taken as electron donors. The *m*-phenylenediamine-chloranil system was studied in detail and outer and inner complexes were found to exist as reaction intermediates. The structure and stability of the inner complex were discussed. Kinetic studies were made for the *m*-phenylenediamine-chloranil and 1,3,5-triaminobenzene-chloranil systems. The enthalpy change, ΔH, for the formation of the outer complex was determined from the temperature dependence of the equilibrium constant. The activation energies, ΔE_1 and ΔE_2, for the processes from the outer complex to the inner complex and from the inner complex to the succeeding intermediate, respectively, were determined by analysing the time dependence of the absorption-peak intensity of the inner complexes measured at several temperatures. The results are as follows: $\Delta H = -3.7$, $\Delta E_1 = 10$, and $\Delta E_2 = 22$ (kcal/mol) for the *m*-phenylenediamine-chloranil system; $\Delta H = -2.6$, $\Delta E_1 = 16$, and $\Delta E_2 = 14$ (kcal/mol) for the 1,3,5-triaminobenzene-chloranil system.

The aromatic substitution reaction has hitherto been extensively studied.[1] There still remain, however, some important problems unsolved. For instance, the role of the outer (π) and inner (σ) complexes has been discussed by many authors, but is still in dispute.[2]

One of the present authors (S. N.) previously presented the charge-transfer mechanism of the aromatic substitution reaction[3] on the basis of Mulliken's concept[4] on the electron donor-acceptor interaction. In order to clarify further this problem from the experimental point of view, we have carried out several

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[1] R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Co., Amsterdam (1965); "Organic Reaction Mechanism," An International Symposium, The Chemistry Society, London (1965); S. D. Ross, "Progress in Physical Organic Chemistry," Vol. I, ed. by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, New York, N. Y. (1963), p. 1; E. Berliner, *ibid.*, Vol. II (1964), p. 253; E. Baciocchi and G. Illuminati, *ibid.*, Vol. V (1967), p. 1.

[2] H. C. Brown and J. D. Brady, *J. Amer. Chem. Soc.*, **74**, 3570 (1952); G. A. Olah and J. D. Brady, *ibid.*, **83**, 4571 (1961); R. Nakane, O. Kurihara, and A. Natsubori, *ibid.*, **91**, 4528 (1969).

[3] S. Nagakura, *Tetrahedron*, **19**, Supl. 2, 361 (1963).

[4] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952); R. S. Mulliken and W. B. Person, "Molecular Complexes," John Wiley & Sons, Inc., New York (1969).

experimental studies, taking benzoquinone and its halo-derivatives as electron acceptors. In previous papers of this series, the reactions of aniline[5a] and 1,3,5-triaminobenzene[5b] with chloranil were studied, special attention being paid to the roles of the outer (π) and inner (σ) complexes in the reaction. The present paper is concerned with several systems containing meta-substituted derivatives of aniline and chloranil. The *m*-phenylenediamine-chloranil system was studied in particular detail in order to clarify the reaction mechanism and to determine the potential energy curve for the reaction.

Experimental

Materials. 1,3,5-Triaminobenzene, 1-methyl-2,4,6-triaminobenzene, and *N,N*-dimethyl-*m*-phenylenediamine were synthesized by reducing the corresponding nitro compounds catalytically.[6] They were purified by vacuum sublimation. Commercially-available *m*-aminophenol and *m*-phenylenediamine (abbreviated to *m*-PD) were also purified by the same method. Chloranil was purified by repeated recrystallizations from acetone.

Measurements. A Cary recording spectrophotometer model 14 M was used for the measurements of ultraviolet and visible absorption spectra, a quartz cell of 1 cm path length being used. The donor and acceptor solutions, which were separately prepared, were mixed with each other immediately before the absorption measurements. For the measurements at low temperatures, a sample cell was cooled with dry ice-acetone in a quartz dewar vessel designed for the spectroscopic measurements.

The temperature dependence of the equilibrium constant of the outer complex was measured in the range from −84°C to −93°C.[7] For this purpose, a sample cell was immersed in the dewar vessel and was cooled with cold nitrogen gas. The temperature was regulated by the nitrogen-flow velocity. The rate constants for the reaction processes from the outer complex to the inner complex and from the inner complex to the succeeding intermediates, were measured in the temperature range from 9.5 to 25.5°C. The temperature of a sample cell in the dewar vessel was regulated by circulating thermostated water.

Results and Discussion

Temperature or Time Dependence of the Electronic Absorption Spectrum of the m-*PD-chloranil System.* After mixing the acetone solution of *m*-PD with that of chloranil at −80°C (*m*-PD, 2.0×10^{-3} M; chloranil, 1.0×10^{-3} M), the reaction process was studied by measuring the absorption spectra at various stages. The results are shown in Fig. 1. A band at 680 mμ (curve 1) measured immediately after mixing at low temperatures is assigned to the outer complex for the following reasons. The peak position is consistent with the value expected for the *m*-PD-chloranil system from a comparison with the CT band positions observed for the chloranil and trinitrobenzene complexes with several aromatic amines. Furthermore, the band intensity below −80°C changes reversibly with increasing and decreasing temperature, and the equilibrium constant for the 1 : 1 complex formation can be obtained, as will be described later, from the concentration dependence of the absorption intensity of the 680 mμ band. This means that the band is due to the outer 1 : 1 complex.

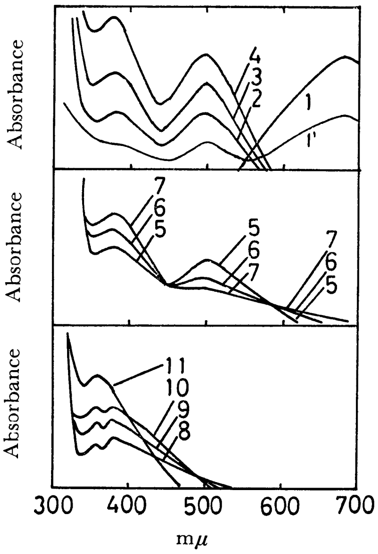

Fig. 1. The absorption spectra of the system containing *m*-PD (2.0×10^{-3} M) and chloranil (1.0×10^{-3} M).

Curve 1: measured at 77°K, immediately after mixing in ethyl ether-isopropyl alcohol (3:1) mixed solvent.

Curve 1′: measured at ~200°K, 10 min after mixing in acetone.

Curves 2—11: measured at room temperature for the acetone solution with the following time intervals after mixing:

6, 14, 25, 32, 46, 62, 90, 217, 374 min, and 28 hr, respectively.

The outer complex is stable below −80°C, but at room temperature it is unstable and the 680 mμ band decreases in intensity. Parallel with the intensity decrease of the 680 mμ band, two new absorption bands appear at 500 mμ and 380 mμ. These two bands increase in intensities for 30 min after the mixing, thereafter, the intensity of the 500 mμ band decreases gradually. This band is assigned to the inner (σ) complex between *m*-PD and chloranil for a reason to be described later.

Even when the 500 mμ band starts to decrease in intensity, the 380 mμ band continues to increase. As may clearly be seen from curves 8—11 in Fig. 1, a new band appears at 355 mμ, parallel with the decrease in the intensity of the 380 mμ band. This new band is due to the final product, the 2(*m*-PD) : 1 (chloranil) substitution product, as will be described later. This experimental result shows that the 380 mμ band is due to the reaction intermediate (P_1) between the inner (σ) complex and the final reaction product,

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[5a] T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969) (Part I of this series).

[5b] T. Yamaoka and S. Nagakura, This Bulletin, **43**, 355 (1970) (Part II of this series).

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

[7] The temperature range is limited by the instability of the outer complex and also by the solidification of the acetone solution. In order to obtain accurate results within these limitations, we took as many points as possible in the range from −84°C to −93°C.

2,5-dichloro-3,6-di-*m*-aminoanilino-*p*-benzoquinone (P_2). A similar phenomenon was observed for the triaminobenzene-chloranil system.[5b] In this system, the intermediate corresponding to P_1 was isolated as a pure crystal and was identified as the 1 : 1 substitution product, 2,5,6-trichloro-3-triaminobenzo-*p*-benzoquinone from the elemental analysis and also from the NMR spectrum. By an analogy with this P_1 in the present case may be identified as 2,3,5-trichloro-6-*m*-aminoanilino-*p*-benzoquinone (see Fig. 2). The mixture of *m*-PD and chloranil with the concentration ratio of *m*-PD: chloranil=1 : 5 exhibits the 380-mμ band even after it has been kept for 24 hours at room temperature. This supports the above assignment, because the reaction from the 1 : 1 species (P_1) to the 2 : 1 species (P_2) may be expected to proceed hardly at all in this case where the concentration of chloranil is much larger than that of *m*-PD. The P_1 species has another weak and broad absorption band extending over nearly the whole range of the visible region and with its absorption peak at 630 mμ.

After 28 hours the reaction has almost completely finished, producing the final reaction product with its absorption peak at 355 mμ. It is identified as 2,5-dichloro-3,6-di-*m*-aminoanilino-*p*-benzoquinone ($C_{18}H_{14}Cl_2N_4O_2$) from the elemental analysis[8] and the NMR spectrum.[9]

An absorption spectrum due to the inner (σ) complex similar to the 500 mμ band observed for the *m*-PD-chloranil system was found for several systems containing chloranil and meta-derivatives of aniline, such as *m*-aminophenol, *N*,*N*-dimethyl-*m*-phenylenediamine and 1-methyl-2,4,6-triaminobenzene. Furthermore, the temperature and time dependencies of the absorption spectra observed for these systems are similar to those for the *m*-PD-chloranil system. This seems to mean that the above reaction mechanism holds for the systems containing *m*-derivatives of aniline as electron donor.

The Spectrum and Structure of the Inner (σ) Complex. For all the systems containing chloranil and the *m*-derivatives of aniline studied here, the absorption peak appears at ~500 mμ in the intermediate stage between the outer (π) complex and the 1 : 1 species corresponding to P_1. By an analogy with the corresponding intermediate in other ring-substitution reactions like the nitration, alkylation, and sulfonation of aromatic hydrocarbons, the intermediate with the peak at 500 mμ may be identified as the inner (σ) complex shown in Fig. 2. In this complex, one of the ring-carbon atoms of chloranil taking the sp^3 hybridization forms a new bond with an aromatic amine and is excluded from the conjugated system. Therefore, we can explain the finding that aromatic amines attached to this carbon have hardly any influence on the absorption spectra of the inner complexes.

Benzoquinone also forms inner complexes with several meta-substituted derivatives of aniline in ethanol, and their absorption peaks (λ_{max}=490 mμ) are almost the same as those for the chloranil complexes. We calculated lower transition energies for the inner (σ) complex between aromatic amine and benzoquinone, assuming the structure shown in Fig. 2. The details of the calculation will be described in the Appendix. The calculated transition energies are 2.14, 4.57, 5.19, 6.55, 6.59, and 7.55 eV. The observed value, 2.53 eV, coincides well with the lowest transition energy calculated. This seems to support the assignment of the 500 mμ band.

Another tentative structure of the inner complex is that an aromatic amine combines with chloranil on one of its ring carbon atoms (see σ' in Fig. 2). This structure, however, may be excluded for the following reason.

The electronic absorption spectrum of the inner complex has no band in the position expected for the benzenium ion-type species of the respective donors. Table 1 shows the peak positions of the ring-protonated and amino-protonated aromatic amines.[10] The ring-protonated aromatic amines exhibit a characteristic band at ~360 mμ. Since the σ' species in Fig. 2 consists of the π-electron system, which is similar to the corresponding ring-protonated aromatic amine, it may be expected to have the characteristic band at ~360 mμ. In actuality, however, the absorption spectrum of the inner complex has no band in the expected position. Therefore, we can exclude the possibility that the inner complex has the structure of σ' in Fig. 2. The fact that P_2 is obtained as the final product also supports the above conclusion as to the structure of the inner (σ) complex.

Contribution of the Outer Complex to the Reaction. Electrophilic aromatic substitution reactions are known to involve both the outer and inner complexes as reaction intermediates.[11] However, it is not well establish-

TABLE 1. THE PEAK POSITIONS OF THE RING AND AMINO PROTONATED AROMATIC AMINES

Amine	Position of protonation	Peak position (mμ)		
1,3,5-Triaminobenzene	ring	365	272	220
	amino	290	220	
N,*N*-Dimethyl-*m*-phenylenediamine	ring	360		
	amino	290	240	
m-Phenylenediamine	ring	360		
	amino	290	240	

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[8] Found: C, 58.26; H, 4.43; Cl, 18.96; N, 14.41%. Calcd for $C_{18}H_{14}Cl_2N_4O_2$: C, 55.53; H, 3.59; Cl, 18.25; N, 14.39%. The discrepancy between the results of the elemental analysis and the calculated values is due to the existence of small amounts of impurities, for example, the 1 : 1 species and HCl salt of *m*-PD. We tried to purify the sample by chromatography and recrystallization techniques, but we were not successful mainly because of the very small solubility of the sample.

[9] The NMR spectrum of the reaction product shows a signal due to the proton of the secondary amine (τ_H=3.05 ppm). This fact shows that the substitution reaction occurs on the amino group.

[10] T. Yamaoka, H. Hosoya, and S. Nagakura, *Tetrahedron*, **26**, 4125 (1970).

[11] R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier Publishing Company, New York (1965).

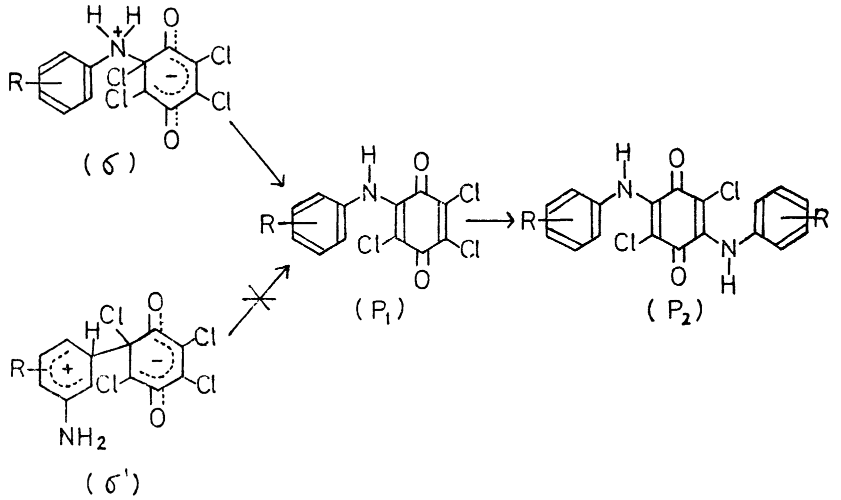

Fig. 2. The structures of the inner complexes ((σ) and (σ')) and the reaction products (P_1 and P_2).

ed whether the outer complex takes part in the main reaction as an intermediate or in a side reaction. The former and latter cases are referred to as "Reaction 1" and "Reaction 2", respectively.

Reaction 1:

$$D + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \pi \xrightarrow{k_3} \sigma \xrightarrow{k_4} \cdots \rightarrow P$$

Reaction 2:

$$\pi \underset{k_1'}{\overset{k_2'}{\rightleftharpoons}} D + A \xrightarrow[k_3']{} \sigma \xrightarrow[k_4']{} \cdots \rightarrow P$$

Here, D,A,π,σ, and P denote aromatic amine, chloranil, the outer complex, the inner complex, and the final reaction product, respectively. The rate constant for each process is indicated by k_i or k_i'. The ΔH, ΔE_1, and ΔE_2 values are the enthalpy change for the formation of the outer complex, the activation energy from π to σ, and that from σ to the succeeding reaction intermediate, respectively. These notations are used throughout this paper.

Since $k_1[D]_0$ ($[D]_0$ is the initial concentration of the donor) and since k_2 are generally much larger than k_3 and k_4 (or $k_1'[D]_0$, $k_2' \gg k_3'[D]_0$, k_4'), it is difficult to determine which of Reaction 1 or Reaction 2 actually occurs. In connection with this, experimental studies of the Friedel-Crafts reaction are worthy of notice.[12] The reaction was found to occur only when the outer complex is formed; *o*-xylene, which forms the outer complex with *t*-C_4H_9Cl-BF_3, causes the butylation reaction, but *p*-xylene, which does not form it, is insusceptible to the Friedel-Crafts reagent. These facts show that the outer complex takes part in the Friedel-Crafts reaction.

Another suggestive fact concerning this problem was found by us for the *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine(TMPD)-chloranil system in an ether-isopropyl alcohol (3 : 1) mixed solvent.[13] We can not detect the inner complex when the system of appropriate concentrations of the component molecules, for which the outer complex formation is negligibly small at room temperature, is cooled directly to the temperature of dry ice-acetone. However, the inner complex is formed by raising the temperature of the system to the dry ice-acetone temperature after it has once been cooled to the liquid nitrogen temperature, at which a considerable amount of the outer complex is formed. This seems to indicate that the inner complex can not be formed directly from the component molecules, but only *via* the outer complex. This finding suggests that Reaction 1 is more probable than Reaction 2. Therefore, we carry out kinetic study taking the path of Reaction 1.

Kinetic Study of the Reaction. The rate equations for Reaction 1 are as follows:

$$\frac{d[A]}{dt} = k_2[\pi] - k_1[D][A] \tag{1}$$

$$\frac{d[\pi]}{dt} = k_1[D][A] - (k_2+k_3)[\pi] \tag{2}$$

$$\frac{d[\sigma]}{dt} = k_3[\pi] - k_4[\sigma] \tag{3}$$

These equations are solved under the following two reasonable conditions;

(a) The concentration of D, [D], is much larger than that of A, [A],[14] and is considered to be approximately equal to the initial concentration, $[D]_0$, throughout the reaction.

(b) Since

$$k_1[D]_0,\ k_2 \gg k_3,\ k_4, \tag{4}$$

a preliminary equilibrium exists between the component molecules and the outer complex with the equilibrium constant, K;

$$K = \frac{[\pi]}{[D][A]} \approx \frac{k_1}{k_2} \tag{5}$$

From Eqs. (1), (2) and condition (a), the following differential equation for $[\pi]$ is derived:

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[12] G. A. Olah, S. H. Flood, and M. E. Moffat, *J. Amer. Chem. Soc.*, **86**, 1060 (1964); R. Nakane, A. Natsubori, and O. Kurihara, *ibid.*, **87**, 3597 (1965); R. Nakane and A. Natsubori, *ibid.*, **88**, 3011, (1966); R. Nakane, T. Oyama, and A. Natsubori, *J. Org. Chem.*, **33**, 275 (1968).

[13] The details will be published in near future.

[14] In our experiment, [D]=40[A].

$$\frac{\mathrm{d}^2[\pi]}{\mathrm{d}t^2} + (k_1[\mathrm{D}]_0 + k_2 + k_3)\frac{\mathrm{d}[\pi]}{\mathrm{d}t} + k_1k_3[\mathrm{D}]_0[\pi] = 0 \tag{6}$$

Considering the boundary condition $(\mathrm{d}[\pi]/\mathrm{d}t)_{t=0} = k_1[\mathrm{D}]_0[\mathrm{A}]_0 - (k_2+k_3)[\pi]_0$, we can obtain the equation for $[\pi]$:[15]

$$[\pi] = p\mathrm{e}^{-\alpha t} + q\mathrm{e}^{-\beta t} \tag{7}$$

Here, $p = \dfrac{k_1[\mathrm{D}]_0[\mathrm{A}]_0 - (k_2+k_3-\beta)[\pi]_0}{\beta-\alpha}$

$$q = \frac{(k_2+k_3-\alpha)[\pi]_0 - k_1[\mathrm{D}]_0[\mathrm{A}]_0}{\beta-\alpha}$$

$$\begin{pmatrix}\alpha\\ \beta\end{pmatrix} = \frac{1}{2}\Big\{k_1[\mathrm{D}]_0 + k_2 + k_3 \mp \sqrt{(k_1[\mathrm{D}]_0+k_2+k_3)^2 - 4k_1k_3[\mathrm{D}]_0}\Big\} \tag{8}$$

By substituting Eq. (7) into Eq. (3) and considering $[\sigma]_0=0$, we can obtain the equation for $[\sigma]$:

$$[\sigma] = \frac{pk_3}{k_4-\alpha}(\mathrm{e}^{-\alpha t} - \mathrm{e}^{-k_4 t}) + \frac{qk_3}{k_4-\beta}(\mathrm{e}^{-\beta t} - \mathrm{e}^{-k_4 t}) \tag{9}$$

The approximate forms of Eqs. (7), (8), and (9) can be derived by adopting Eqs. (4) and (5) as follows:[16]

$$\alpha \approx \frac{k_3K[\mathrm{D}]_0}{K[\mathrm{D}]_0+1} \tag{8$'$}$$

$$\beta \approx k_1[\mathrm{D}]_0 + k_2$$

$$[\pi] \approx p\mathrm{e}^{-\alpha t} \tag{7$'$}$$

$$[\sigma] \approx \frac{pk_3}{k_4-\alpha}(\mathrm{e}^{-\alpha t} - \mathrm{e}^{-k_4 t}) \tag{9$'$}$$

Eqs. (8)′ and (9)′ are used to obtain the activation energies, ΔE_1 and ΔE_2. Furthermore, we can derive the following equation from Eq. (9);

$$\int_0^\infty I_\sigma \mathrm{d}t = \frac{k_1[\mathrm{D}]_0[\mathrm{A}]_0 + (\alpha+\beta-k_2-k_3)[\pi]_0}{k_1k_4[\mathrm{D}]_0} \times \varepsilon_\sigma L \approx \frac{\varepsilon_\sigma L[\mathrm{A}]_0}{k_4} \tag{10}$$

Here, ε_σ and I_σ denote the molar extinction coefficient and absorbance observed with the inner complex, respectively, and L is a light-path length. Equation (10) shows that ε_σ is obtained by measuring the time dependence of I_σ for the inner complex, the I_σ-t curve.

Potential Energy Curve of the Reaction. The *m*-PD-chloranil and TAB-chloranil systems were taken up for the purpose of determining the potential energy curve of the reaction, because the inner complexes in these systems are fairly stable, even at room temperature,[5b] and because the changes in their concentrations with the time can be easily followed by electronicabsorption measurements. We chose the acetone solution for the purpose of determining the potential energy curves, because the main reaction product in this solvent consists of only one species, 2,5-dichloro-3,6-di-*m*-aminoanilino-*p*-benzoquinone, when there is much more *m*-PD than chloranil. On the other hand, at least two main reaction products were found in such solvents as ethyl ether, ethanol, and an ether-isopropyl alcohol mixed solvent, and the reaction mechanism in these solvents seems to be more complicated than that in acetone.

Let us start from the determination of the enthalpy (ΔH) and entropy (ΔS) changes for the outer-complex formation. The absorbance values at the peak position (680 mμ) of the CT band of the outer complex were measured for acetone solutions including various concentrations of *m*-PD and chloranil. The peak molar extinction coefficient, $\varepsilon_{\max}$, was determined to be 3120 M^{-1}cm^{-1} from the Benesi-Hildebrand plot[17] measured at −80°C. Assuming $\varepsilon_{\max}$ to be independent of temperature, the temperature dependence of the equilibrium constant of the outer complex was determined in the range from −84°C to −93°C in the same way as has been described previously.[5a] The ΔH and ΔS for the *m*-PD-chloranil system in acetone were determined to be −3.7 kcal/mol and −13.7 cal/mol·deg, respectively.

The outer complex of the TAB-chloranil system has its absorption peak at 660 mμ in acetone.[5b] The complex is unstable even at temperature of dry ice-acetone, and it is difficult to obtain $\varepsilon_{\max}$ from the Benesi-Hildebrand plot at a low temperature. Therefore, $\varepsilon_{\max}$ of the outer complex for this system was estimated to be 2770 M^{-1}cm^{-1} from the reasonable relation: $(I_{\max})_{m\text{-PD}}/(I_{\max})_{\text{TAB}} = (\varepsilon_{\max})_{m\text{-PD}}/(\varepsilon_{\max})_{\text{TAB}}$. Here, $(I_{\max})_{m\text{-PD}}$ and $(I_{\max})_{\text{TAB}}$ are, respectively, the maximum absorbances of the outer complexes measured at −196°C for the *m*-PD-chloranil and TAB-chloranil systems with equal concentrations of chloranil. Since chloranil is almost completely complexed in both solutions, the concentrations of the outer complexes are expected to be almost equal to each other. By the aid of this value, ΔH and ΔS for the TAB-chloranil system in acetone were determined to be −2.6 kcal/mol and −5.4 cal/mol·deg, respectively.

Immediately after mixing acetone solution of each electron donor with that of chloranil ($[m\text{-PD}] = [\text{TAB}] = 2.0\times10^{-2}$ M, $[\text{chloranil}] = 5.0\times10^{-4}$ M), we started the measurement of I_σ and obtained the I_σ-t curves at several temperatures. Both the systems gave curves which fit in well with Eq. (9)′. Figure 3 shows the result observed at 15.8°C for the *m*-PD-chloranil system. By analysing the experimental results by the aid of Eq. (9)′, the temperature dependences of α and k_4 were obtained. Furthermore, k_3 was obtained from

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15) An initial concentration is represented by attaching the suffix 0.

16) The rate equations for Reaction 2 can be solved definitely by the same procedures as have been described above. The final approximate forms are as follows:

$$[\pi] \approx p'\mathrm{e}^{-\alpha' t} \tag{11}$$

$$[\sigma] \approx \frac{k_3'[\mathrm{D}]_0q'}{k_4'-\alpha'}(\mathrm{e}^{-\alpha' t} - \mathrm{e}^{-k_4' t}) \tag{12}$$

$$\alpha' \approx \frac{k_3'[\mathrm{D}]_0}{1+K[\mathrm{D}]_0} \tag{13}$$

$$\beta' \approx (k_1'+k_3')[\mathrm{D}]_0 + k_2'$$

Here, $p' = \dfrac{k_1'[\mathrm{D}]_0[\mathrm{A}]_0 + (\beta'-k_2')[\pi]_0}{\beta'}$

$$q' = \frac{k_2'[\pi]_0 - (k_1'[\mathrm{D}]_0 + k_3[\mathrm{D}]_0 - \beta')[\mathrm{A}]_0}{\beta'}$$

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

α by the aid of Eq. (8)′, K being estimated by extrapolating the $\log K$-$1/T$ relation obtained at low temperatures. The values of k_3 and k_4 thus obtained are tabulated in Table 2. From the Arrhenius plot of these results, ΔE_1 and ΔE_2 were determined; the results are given in Table 3.[18]

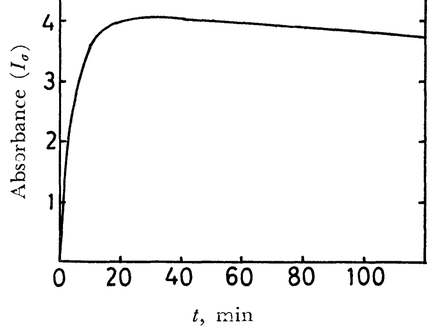

Fig. 3. The time-dependence of the absorption peak intensity observed at 15.8°C for the inner complex between *m*-phenylenediamine and chloranil.

TABLE 2. TEMPERATURE DEPENDENCE OF k_3 AND k_4 (in sec^{-1}) FOR THE *m*-PHENYLENEDIAMINE-CHLORANIL AND 1,3,5-TRIAMINOBENZENE-CHLORANIL SYSTEMS

m-PD-Chloranil	15.8°	20.8°	25.5°
$k_3\times 10$	2.55	3.33	4.65
$k_4\times 10^5$	3.52	5.93	12.20
TAB-Chloranil	9.5°	17.7°	22.5°
k_3	1.07	1.69	3.91
$k_4\times 10^5$	1.92	5.27	6.06

TABLE 3. THE ΔH, ΔE_1 AND ΔE_2 VALUES (in kcal/mol) FOR THE *m*-PHENYLENEDIAMINE-CHLORANIL AND 1,3,5-TRIAMINOBENZENE-CHLORANIL SYSTEMS

	m-PD-Chloranil	TAB-Chloranil
ΔH	−3.7	−2.6
ΔE_1	10	16
ΔE_2	22	14

Figure 4 shows schematically the potential energy curves of the reactions for the *m*-PD-chloranil and TAB-chloranil systems. The structures of P_1 and P_2 are shown in Fig. 2; σ_1 corresponds to σ in the same figure. σ_2, the inner (σ) complex between P_1 and *m*-PD, is tentatively assumed to exist as an intermediate between P_1 and P_2, though it has not yet been observed. The potential energy curves from P_1 to P_2, the parts drawn by broken lines in Fig. 4, are difficult to be investigated for the following two reasons: (1) The σ_2 can not be detected by an electronic absorption measurement, and (2) the absorption bands due to P_1 and P_2 overlap with each other, so the time dependenc of the absorption peak intensity is difficult to be obtained separately for each band.

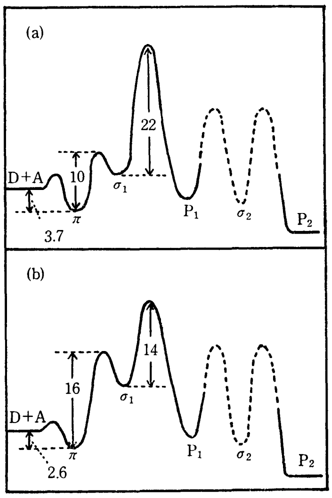

Fig. 4. Experimentally determined potential energy curves for the reactions: (a) between *m*-phenylenediamine and chloranil, (b) between 1,3,5-triaminobenzene and chloranil (unit, kcal/mol).
In both systems, the potential energy curves from P_1 to P_2 could not be determined.

None of the inner complexes formed between aromatic amines under consideration and chloranil can be isolated stably, and their molar extinction coefficients ($\varepsilon_{\mathrm{max}}$'s) can not be determined directly. The $\varepsilon_{\mathrm{max}}$'s value of the *m*-PD-chloranil system was estimated to be 8600 $\mathrm{M}^{-1}\mathrm{cm}^{-1}$ by applying Eq. (10) to the I_σ-t curve measured at 25°C.

Rate-determining Step of the Reaction. In the *m*-PD-chloranil and TAB-chloranil systems, the rate for the outer-complex formation ($k_1[\mathrm{D}]_0$) is probably 10^7 (sec^{-1}) or larger.[18] On the other hand, k_3 and k_4 are 10^0 and 10^{-5} (sec^{-1}), respectively. In actuality, the outer-complex formation is very fast in the reactions under consideration, and it is clear that the inner (σ) complex plays an important role in the rate-determining step. Therefore, it is concluded that Brown's view is the more appropriate to the present systems.

Stability of the Inner Complex. A parallel relationship exists between the electron-donating ability of the meta-substituent group of aniline and the stabilities of the inner complexes; *i.e.*, the following order of the stabilities of the inner complex was found:

m-anisidine(a few seconds) < *m*-aminophenol (a few minutes) < *m*-PD ≈ *N,N*-dimethyl-*m*-PD ≈ *s*-TAB ≈ 1-methyl-2,4,6-TAB (a few hours) ≪ *N,N,N′,N′*-tetramethyl-*m*-PD (about five days). Here, the time in parentheses indicate the approximate duration of existence for the corresponding inner complex at room temperature.

These facts can be explained as follows. With the increasing electron-donating ability of the meta-substituent, the electron-migration from the amino group to the benzene ring decreases and the nonbonding electron density on the nitrogen atom increases. Thus, chloranil may be expected to form a more stable inner complex with the meta-derivatives of aniline with stronger electron-donating groups.

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[18] These values are estimated by assuming a diffusion-controlled reaction.

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Appendix

Calculation of the Electronic Structure of the Inner Complex. We studied theoretically the π-electron structures of the inner complex between benzoquinone and aromatic amine by method combining the CI procedure with the Pariser-Parr-Pople type SCF MO,[19] taking a model of the negative ion in which one of the six ring carbon atoms of benzoquinone is excluded from the conjugated system. In actual calculation, the bond lengths of the ion were taken to be equal to those of benzoquinone.[20] The transition energies were evaluated by the aid of a HITAC 5020E electronic computer at the Computer Centre, The University of Tokyo. The ionization potentials, I_p's, and electron affinities, E_a's of carbon, nitrogen. and oxygen in their valence states were taken from Pilcher-Skinner's table.[21] The core resonance integral, $\beta_{\mathrm{X-Y}}$, was considered only for the nearest neighbours. These quantities are taken to be as follows:

$$I_{\mathrm{C}} = 11.2\,\mathrm{eV},\ I_{\mathrm{N}} = 28.88\,\mathrm{eV},\ I_{\mathrm{O}} = 17.25\,\mathrm{eV},$$

$$E_{\mathrm{C}} = 0.6\,\mathrm{eV},\ E_{\mathrm{N}} = 12.25\,\mathrm{eV},\ E_{\mathrm{O}} = 2.58\,\mathrm{eV},$$

$$\beta_{\mathrm{C-C}} = -2.39\,\mathrm{eV},\ \beta_{\mathrm{C-N}} = -2.60\,\mathrm{eV},\ \beta_{\mathrm{C=O}} = -2.60\,\mathrm{eV}.$$

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