

As for the direction of the principal value g_1 , which may correspond to the half-filled $2p-\pi$ orbital on the oxygen atom, it might be expected to lie in the COO plane, or to be perpendicular to it, from the symmetry of the radical. However, the direction of the $2p-\pi$ orbital determined from these experiments is neither in the COO plane nor perpendicular to it. It was shown from the experimental direction that the half-filled $2p-\pi$ orbital on the oxygen atom makes an angle of 27° from the COO plane. The deviation of 27° from the COO plane may be caused by the interaction of the unpaired electron with the CONH_2 group in the radical and/or that with the neighboring molecules.

Conclusion

The esr spectra and the structure of the peroxy rad-

ical trapped in an organic simple molecule have been studied using single crystals of trifluoroacetamide. The marked temperature change of the observed \mathbf{g} tensor has been satisfactorily interpreted as resulting from rapid rotation around the C-O bond at room temperature. The approximate structure of the peroxy radical has been determined from the principal directions of its \mathbf{g} tensor and the α -fluorine hyperfine tensor of the forerunner radical $\cdot\text{CF}_2\text{CONH}_2$. It was concluded that the O-O bond in the peroxy radical lies nearly parallel to the plane of the forerunner radical and that the conformation of the O-O bond to the C-C bond is *trans*. This structure is quite reasonable if one supposes that the oxygen molecule bonds with the half-filled $\text{C}_{2p-\pi}$ orbital of $\cdot\text{CF}_2\text{CONH}_2$ without causing any change of the mother radical structure except the change in hybridization of the orbital of the radical carbon.

Charge-Transfer Interaction and Chemical Reaction. I.

Reaction of Aniline with Chloranil

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The interaction of aniline with chloranil in mixed solvent of ether-isopropyl alcohol (3:1) was studied by measuring ultraviolet, visible, and infrared absorption spectra at various temperatures ranging from 36°K to room temperature. The (π, π) type outer complex was found to exist stably in an equilibrium with the component molecules at low temperatures below $\sim 200^\circ\text{K}$. The equilibrium constant was determined by the aid of the Benesi-Hildebrand equation at several temperatures between 115 and 195°K . The heat of formation and entropy change of the complex were evaluated to be -2.1 (kcal/mol) and -7.2 (cal/deg mol), respectively, from the temperature dependence of the equilibrium constant. With increasing temperature the reaction proceeds yielding 2,5-dichloro-3,6-dianilino-*p*-benzoquinone as a reaction product. The reaction mechanism through inner (σ) complexes was proposed and discussed.

Introduction

Since Mulliken presented the well-known theory¹ of the charge-transfer (abbreviated hereafter to CT) interaction between electron donor and acceptor, it has been successfully and widely applied to many interesting research subjects.² One of them is the possible role of CT complexes in chemical reactions.³ CT complexes are known to take part in many reactions such as addition, substitution, and condensation reactions.

One of the detailed studies carried out so far on this line is that by Rappoport,⁴ who investigated the system including *N,N*-dimethylaniline as an electron donor and

tetracyanoethylene as an electron acceptor. He presented the following scheme as the reaction path of this system.

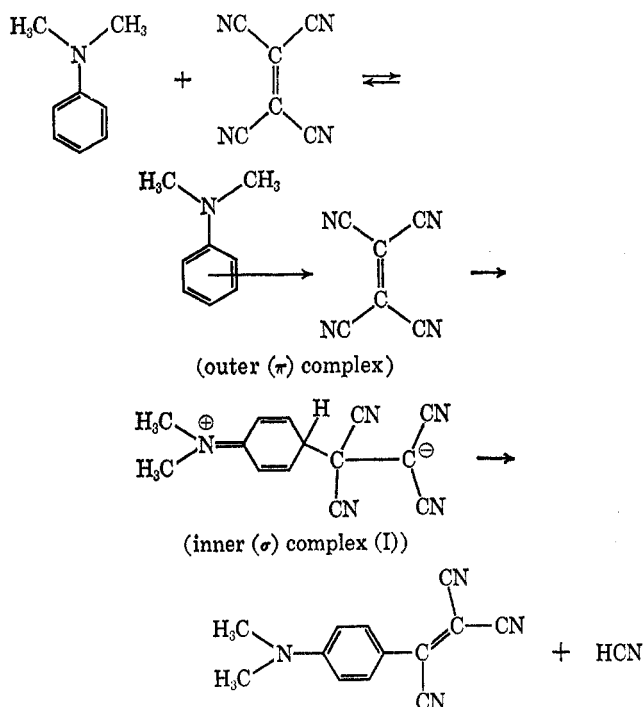
Recently, White, *et al.*, measured the ultraviolet, visi-

(1) R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

(2) G. Breigreb, "Elektronen - Donator - Acceptor - Komplexe," Springer-Verlag, Berlin, 1961. L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964.

(3) For a review of this subject, see E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965).

(4) Z. Rappoport, *J. Chem. Soc.*, 4498 (1963).



ble, and infrared absorption spectra and the nmr spectrum of the inner (σ) complex in this system⁵ and determined its structure to be (I) in accordance with the Rapoport assumption. Although similar studies have also been carried out for several other systems, the important problem whether outer (π) complexes are formed in independent side reactions or whether they are essential intermediates is still a matter of controversy and is left to be solved experimentally in the future. Under these circumstances, we have undertaken to study in detail the CT interaction for various systems containing electron donors and acceptors, paying special attention to the contribution of outer (π) and inner (σ) complexes to reaction mechanisms.

Gore and Wheals^{6a} and also Mukherjee and Chandra^{6b} independently investigated the CT interaction of chloranil with aromatic amines such as aniline and its methyl derivatives by the aid of electronic absorption spectra. They observed the CT absorption bands characteristic of the (π, π) type outer complex and discussed the relation of their peak positions to the electron-donating ability of aromatic amines. On the other hand, some aromatic amines, for example aniline, are known to cause a nucleophilic substitution reaction with chloranil under drastic conditions. Therefore, aromatic amine-chloranil systems may be regarded as typical examples suitable to study the role of CT complexes in the substitution reaction. From this point of view, we have taken the aniline-chloranil system as the first example in a series of investigations.

Experimental Section

Chloranil and aniline were purified by repeated recrystallizations from acetone and by vacuum distillation, respectively. Ethyl ether used as a solvent was

purified by distillation after dehydration by sodium. Commercially available isopropyl alcohol was used without further purification.

Visible and ultraviolet absorption spectra were measured with a Cary recording spectrophotometer Model 14M and infrared absorption spectra with a Hitachi EPI 2 infrared spectrophotometer. A Hitachi spectrometer (X-band, 100-kc modulation) was used for the measurements of esr spectra.

Temperature was regulated by a Cryo-Tip (Air Products and Chemicals Incorporated).⁷ Precise temperature regulation was possible from 20°K up to about 200°K, but regulation at temperatures higher than 200°K was less accurate. Temperature was measured with a gold-cobalt-copper thermocouple. It took about 60 min to reach liquid hydrogen temperature at the position of a specimen holder starting from room temperature. Quartz cells of 1-cm path length were used throughout our experimental work.

Results and Discussion

The ether-isopropyl alcohol (3:1) solutions of aniline and chloranil were mixed with each other at 77°K, and the temperature dependence of ultraviolet and visible absorption spectra were measured. As is clearly seen in Figure 1, an absorption band appears at 560 $m\mu$ at low temperature. With increasing temperature, this band decreases its intensity and a new absorption band appears at 385 $m\mu$. No other absorption band was observed at the longer wavelength region than 350 $m\mu$ throughout the reaction.

Absorption Band at 560 $m\mu$. The absorption band at 560 $m\mu$ is undoubtedly due to neither aniline nor chloranil from its peak position. When the solution was warmed from 36 to 200°K, the intensity of the band always decreased. Upon recooling to 36°K, the absorption band recovered its original intensity completely. This suggests the existence of a stable equilibrium between the CT complex and the component molecules at low temperatures below 200°K. Furthermore, the observed peak position is well coincident with that of the CT absorption band predicted for the aniline-chloranil complex from the observed ionization potential of aniline (7.69 eV).⁸ These facts support the interpretation that the 560- $m\mu$ band can be regarded as the CT band.

We measured the concentration dependency of the 560- $m\mu$ band intensity at 195°K changing the concentration of aniline in the range of $2.5 \times 10^{-2} \sim 2.0 \times 10^{-1}$ M and keeping the concentration of *p*-chloranil constant (4.0×10^{-3} M). The plots of the reciprocal of the ob-

(5) P. G. Farrell, J. Newton, and P. F. M. White, *J. Chem. Soc.*, 637 (1967).

(6) (a) P. H. Gore and B. B. Wheals, *Anal. Chim. Acta*, **30**, 34 (1964); (b) D. C. Mukherjee and A. K. Chandra, *J. Phys. Chem.*, **68**, 477 (1964).

(7) D. White and D. E. Mann, *Rev. Sci. Instr.*, **34**, 1370 (1963).

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

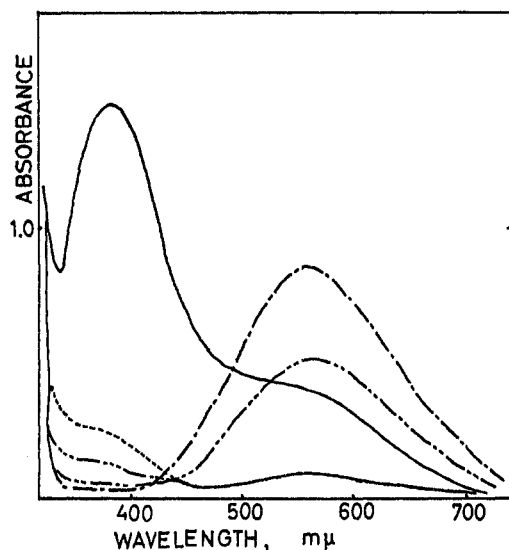


Figure 1. Temperature dependence of the ultraviolet and visible absorption spectra of the aniline-chloranil system in ether-isopropyl alcohol (3:1): aniline, $2.0 \times 10^{-1} M$; chloranil, $2.5 \times 10^{-3} M$; —, 36°K; ----, 83°K; ·····, 182°K; - · - · -, 300°K; after —, keeping at 300°K for 24 hr.

served absorbance⁹ at 560 $m\mu$ against the reciprocal of the concentration of aniline fit well to a straight line within an experimental error, the following Benesi-Hildebrand equation¹⁰ being satisfied

$$\frac{[A]}{a} = \frac{1}{K\epsilon} \frac{1}{[D]} + \frac{1}{\epsilon} \quad (1)$$

Here, a , $[D]$, and $[A]$ denote the absorbance at 560 $m\mu$, the concentration of aniline, and the concentration of chloranil, respectively. K and ϵ are the equilibrium constant and the molar extinction coefficient of the CT band at 560 $m\mu$, respectively. This result leads to the conclusion that a 1:1 CT complex is formed between aniline and chloranil. By the aid of the Benesi-Hildebrand relation, ϵ and K were estimated to be 1250 ($M^{-1} \text{ cm}^{-1}$) and 21 (M^{-1}) at 195°K, respectively. Assuming ϵ independent of temperature, we determined the equilibrium constant of the CT complex at several different temperatures in the region of 115–195°K. That is to say, K can be obtained from the concentrations of the components and the absorbance at 560 $m\mu$ observed at the respective temperatures by the equation

$$K = \frac{a}{(\epsilon[A] - a)[D]} \quad (2)$$

From the temperature dependence of the equilibrium constant, the heat of formation and entropy change of the CT complex were estimated to be -2.1 (kcal/mol) and -7.2 (cal/deg mol), respectively.

Absorption Band at 385 $m\mu$. The absorption band at 385 $m\mu$ which appeared with raising temperature of the

solution containing aniline and chloranil in ether-isopropyl alcohol (3:1) mixed solvent continued to increase its intensity until the end of the reaction. This shows that the band is due to the reaction product. The brown reaction product precipitated 24 hr after mixing the solutions of aniline and chloranil. An elementary analysis of the reaction product corresponds to $C_{18}H_{12}Cl_2N_2O_2$, indicating that two chlorine atoms of chloranil are replaced by two anilino groups.¹¹ To confirm this, we measured ultraviolet, visible, and infrared absorption spectra of the reaction product and compared them with those of 2,5-dichloro-3,6-dianilino-*p*-benzoquinone (abbreviated hereafter to DDB) measured by Draber, *et al.*¹² The satisfactory agreement leads to the conclusion that the reaction product is DDB.¹³

Time Dependence of Absorption Spectra at 0°. We measured at 0° the time dependence of the absorption spectrum of the solution containing aniline and chloranil in ether-isopropyl alcohol (3:1) mixed solvent, with the result shown in Figure 2. This figure shows that the intensity of the 560- $m\mu$ band is almost constant at the initial stage of the reaction,¹⁴ whereas the 385- $m\mu$ band gradually increases its intensity. The similar tendency was observed at several temperatures above 200°K, whenever the temperature was kept constant. This is because the reaction product (DDB) has a weak absorption band (ϵ 700) at 550 $m\mu$ ¹² in addition to the strong 385- $m\mu$ band. The increase of this band and the decrease of the CT band at 560 $m\mu$ (ϵ 1250) may be expected to cancel each other at the initial stage of the reaction.

Reaction Mechanism. One can see from Figure 1 that with increasing temperature from 36°K up to room temperature more rapidly than the formation rate of the reaction product, the absorption band at 560 $m\mu$ immediately decreases its intensity. This can be explained by the decrease in the equilibrium constant between the CT complex and its component molecules with increasing temperature. The intensity of the 385- $m\mu$ band hardly changes immediately after the temperature rising and increases gradually after an apparent induction period. These observations suggest that a clear time delay exists between the decay of the outer complex and the formation of the product. This means

(9) The absorbance values are corrected for the volume contraction on cooling.

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

(11) Elementary analysis: Calcd for $C_{18}H_{12}Cl_2N_2O_2$: C, 60.17; H, 3.34; Cl, 19.22; N, 7.80. Found: C, 59.63; H, 3.38; Cl, 20.27; N, 7.79.

(12) K. Wallenfels and W. Draber, *Tetrahedron*, **20**, 1889 (1964). Infrared absorption spectra of DDB: 3279 cm^{-1} (N—H stretching), 1662 cm^{-1} (C=O stretching), 1568 cm^{-1} (C=C stretching), 1496 cm^{-1} , 1453 cm^{-1} . Visible and ultraviolet absorption spectra of DDB: 550 $m\mu$ (ϵ 700), 385 $m\mu$ (ϵ 16,800), 265 $m\mu$ (ϵ 16,000).

(13) Nakazawa synthesized DDB by boiling the ethanol solution of aniline, chloranil, and sodium acetate (S. Nakazawa, *J. Soc. Org. Synth. Chem.* (in Japanese), **21**, 49 (1963)).

(14) Curve 4 corresponds to about 4% product formation.

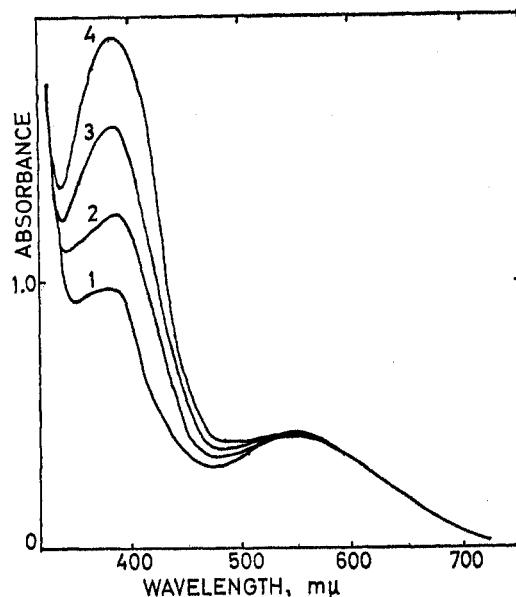
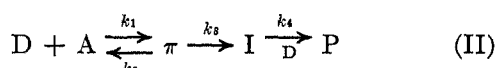
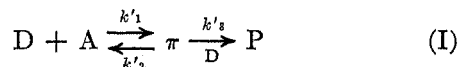


Figure 2. Time dependence of the electronic absorption spectra at 0°: 1, 20 min after mixing the aniline solution with the chloranil solution; 2, 29 min; 3, 37 min; 4, 44 min.

that the rate (k_2, k'_2) of dissociation of the outer (π) complex is much faster than the rate (k_3, k'_3) of its conversion into the product. In this connection, we measured in detail the time dependency of the absorption intensity of the 385-m μ band at 0°. The result shown in Figure 3 was analyzed for the purpose of clarifying the reaction mechanism.

Let us consider the following two reactions.



Here D, A, π , I and P denote aniline, chloranil, the outer (π) complex, intermediate specimens, and the reaction product, respectively. In reaction I, the outer (π) complex directly converts into the product, and no intermediate exists between them. On the other hand, in reaction II, intermediate reaction steps exist between them.

By solving the rate equations on the assumptions given in the Appendix, the concentration of the product can be obtained as follows.¹⁵

$$[P] = \pi_0(1 - e^{-k_3'[D]t}) \quad (\text{for reaction I})$$

$$[P] = \frac{k_3 k_4 [D] \pi_0}{k_3 - k_4 [D]} \left(\frac{e^{-k_3 t} - 1}{k_3} - \frac{e^{-k_4 [D] t} - 1}{k_4 [D]} \right) \quad (\text{for reaction II})$$

Here π_0 is the initial concentration of the outer (π) complex. The relations between $[P]$ and t for reactions I and II are represented in Figure 4. In particular, for reaction II the $[P]$ - t and $[I]$ (intermediate specimen)- t

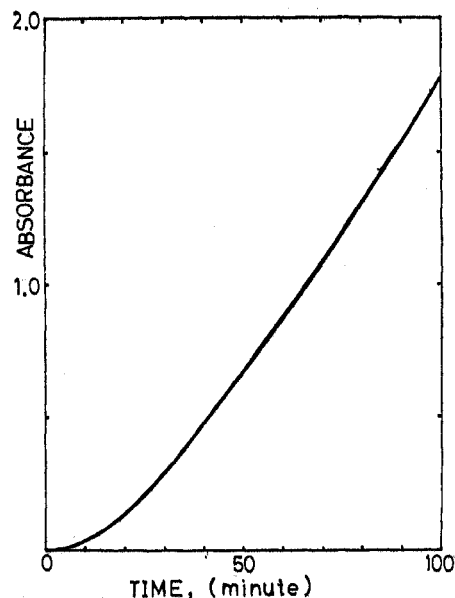


Figure 3. Time dependence of the absorption intensity of the reaction product at 0° in ether-isopropyl alcohol (3:1): aniline, $2.0 \times 10^{-2} M$; chloranil, $1.0 \times 10^{-3} M$.

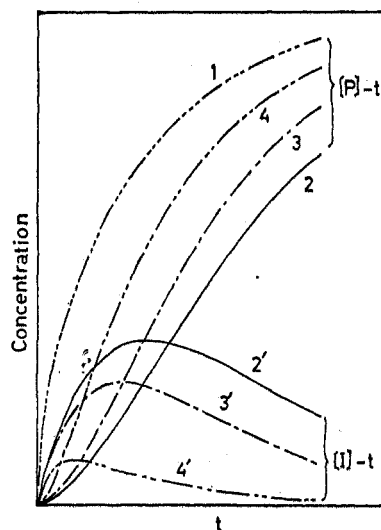


Figure 4. Theoretical time dependencies of the reaction product (P) and reaction intermediates (I): curve 1, for reaction I; curves 2 and 2', in the case of $k_4[D] = 1.2k_3$ for reaction II; curves 3 and 3', in the case of $k_4[D] = 2k_3$ for reaction II; curves 4 and 4', in the case of $k_4[D] = 8k_3$ for reaction II. In our experiment, $[D]$ is $\sim 10^{-2} M$.

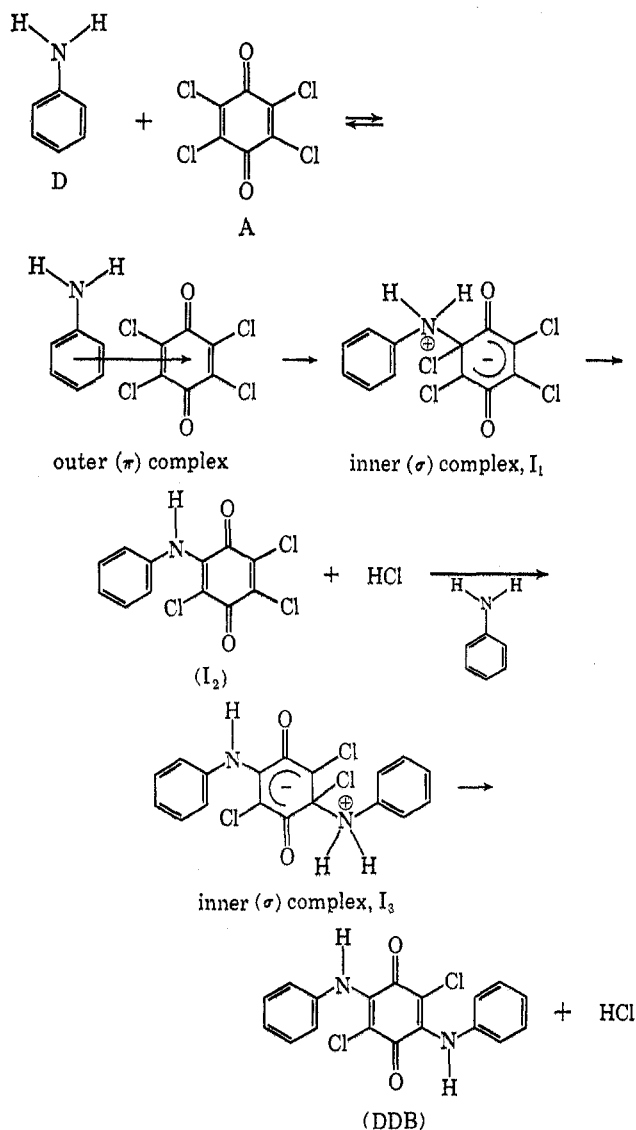
curves are obtained for various values of $k_3:k_4[D]$. In the initial stage, $[P]$ increases linearly and quadratically with respect to t for reactions I and II, respectively. By paying special attention to this point, it is known that the experimental curve shown in Figure 3 corresponds to the $[P]$ - t relation for reaction II. This means

(15) The solution for reaction II holds also for the case where several reaction intermediates (I_1, I_2, \dots, I_n) exist between the outer complex and the reaction product.

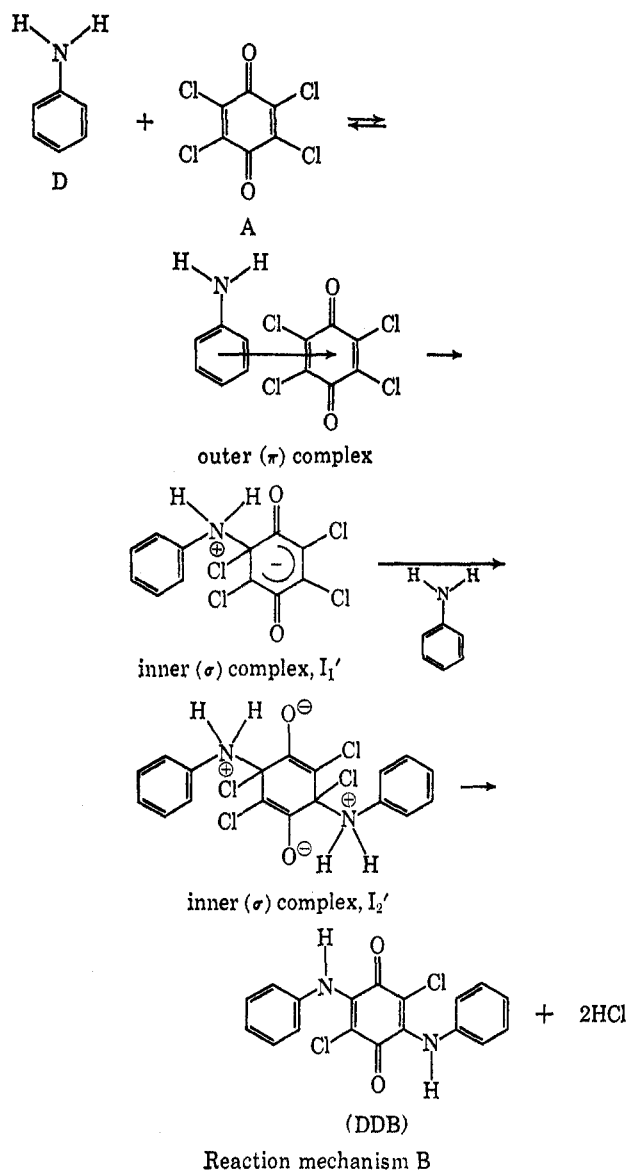
that intermediate reaction steps exist between the outer (π) complex and the reaction product.^{16,17}

We certified the existence of inner (σ) complexes for various complexes consisting of *meta*-substituted anilines and chloranil and found a parallel relationship between the electron donating power of the *meta*-substituted groups and the stability of the corresponding inner (σ) complex,¹⁷ which was found to decrease in the order: 1,3,5-triaminobenzene \geq N,N-dimethyl-*m*-phenylenediamine \approx *m*-phenylenediamine $>$ *m*-aminophenol $>$ *m*-anisidine.

From an analogy with the above-mentioned systems, the inner (σ) complex may be expected to exist as a reaction intermediate also for the aniline-chloranil system. However, we could not detect it by the aid of the absorption spectrum measurement. This may be because it is even less stable than the inner (σ) complex formed between *m*-anisidine and chloranil which is unstable and can exist only for a few seconds even at a temperature as low as 195°K.



From an analogy with the structures of the intermediate inner complexes actually observed for the similar systems and also from the structure of the reaction product, we may expect the following two possibilities for the inner (σ) complexes as the intermediate states of the aniline-chloranil system.¹⁸



The present study cannot provide any answer as to which one is the more reasonable reaction path, mechanism A or B.

Another problem to be left unsolved in the present

(16) An important reason why we cannot detect the reaction intermediate I may, of course, be that its concentration is rather low. Another reason is that the absorption band of the inner (σ) complex, conceivably corresponding to I, may be considered to appear in the wavelength region of 500 m μ ¹⁷ and therefore to be covered by the CT band of the outer (π) complex.

(17) T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, to be published.

(18) Reaction mechanisms through ion radicals as reaction intermediates may safely be disregarded for this system. This is because no esr signal can be detected for the present case.

study is whether or not the outer (π) complex actually takes part in the reaction. This point will be discussed with detail in later papers.¹⁹

Appendix

The Solution of the Rate Equations

The rate equations of reactions I and II can be solved on the following two reasonable assumptions. (1) In the initial stage of the reaction, the concentration of aniline, which is ten times or much more higher than that of chloranil, may be considered to be almost constant. (2) Both k_1 (or k'_1) and k_2 (or k'_2) are much larger than k_3 (or k'_3) and k_4 and therefore a preliminary equilibrium between the outer (π) complex and the component molecules can be assumed.

(1) *Reaction 1.* The rate equations of reaction I are

$$\frac{d[\pi]}{dt} = k'_1[D][A] - k'_2[\pi] - k'_3[\pi][D] \quad (A1)$$

$$\frac{d[P]}{dt} = k'_3[\pi][D] \quad (A2)$$

By the above assumption (2), $k'_1[D][A]$ and $k'_2[\pi]$ on the right-hand side of eq A1 can be cancelled out with each other. Therefore eq A1 is simplified as

$$\frac{d[\pi]}{dt} = -k'_3[\pi][D] \quad (A1')$$

Equations A1' and A2 can be solved easily to be

$$[\pi] = \pi_0 e^{-k'_3[D]t} \quad (A3)$$

$$[P] = \pi_0(1 - e^{-k'_3[D]t}) \quad (A4)$$

(2) *Reaction 2.* The rate equations of reaction II can be solved by analogy with those of reaction I. The solutions are

$$[\pi] = \pi_0 e^{-k_3[D]t} \quad (A5)$$

$$[I] = \frac{k_3[D]\pi_0}{k_4 - k_3[D]} \{e^{-k_3[D]t} - e^{-k_4t}\} \quad (A6)$$

$$[P] = \frac{k_3k_4[D]\pi_0}{k_4 - k_3[D]} \left\{ \frac{1 - e^{-k_3[D]t}}{k_3[D]} - \frac{1 - e^{-k_4t}}{k_4} \right\} \quad (A7)$$

The solutions of (3)–(7) are valid only in the initial stage of the reaction, where the concentration of aniline can be regarded as almost constant.

(19) We measured the change in the absorption intensity with time for the system consisting of 1,3,5-triaminobenzene and chloranil. As the result of the detailed analysis of this experiment, the intermediate inner (σ) complex was found to be produced through the outer complex. Such a phenomenon probably takes place in the aniline-chloranil system, too.