

# Chemical Reactions of Some Aromatic Diamine-Chloranil Complexes at Very High Pressure

Tadayoshi Sakata,\* Akifumi Onodera, Hiroshi Tsubomura, and Naoto Kawai

Contribution from the Departments of Chemistry and Material Physics,  
Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

Received December 31, 1973

**Abstract:** The effect of high pressure up to several hundred kilobars on the electrical and chemical properties of charge transfer complexes between aromatic diamines and *p*-chloranil has been studied. In all cases, the resistance first decreased rapidly with pressure, then rose, and decreased again slowly at still higher pressures. Spectral measurements reveal that chemical reactions take place under high pressure. In the case of *p*-phenylenediamine-chloranil complex, chloranil, tetrachlorohydroquinone, and polyazophenylene are found to be present in the product, and the mechanisms of the reactions are discussed.

The effect of very high pressure on the electrical properties of organic charge transfer (CT) complexes has been studied by several authors.<sup>1-5</sup> It has been found that the resistance generally decreases with increasing pressure and for some compounds it recovers to some extent at higher pressure. For most of the cases, these changes seem to arise from chemical reactions under high pressure, although few reports about the reaction products have been made because of the difficulty in the experiments.<sup>6,7</sup>

The reactions of CT complexes which seem to be taking place under high pressure are interesting not only from the view point of high-pressure chemistry but also from that of CT reaction mechanism in the solid state. The reactions between electron donors and acceptors have been studied so far mainly in solution. The reactions in the solid state under ordinary as well as high pressure are expected to be different from those in solutions.

Nogami and Nagakura<sup>8</sup> studied the CT interaction between *p*-phenylenediamine (PPD) and *p*-chloranil (CA) and reported the formation of 2,5-dichloro-3,6-di-*p*-aminoaniline-*p*-benzoquinone. Bentley and Drickamer reported briefly the effect of pressure for the PPD·CA (3:2) complex.<sup>3</sup>

## Experimental Section

**Preparation of Materials.** Commercial *p*-chloranil (CA) was purified by recrystallization from benzene. *p*-Phenylenediamine (PPD) was recrystallized from benzene until colorless crystalline solid was obtained. Commercial *N,N'*-dimethyl-*p*-phenylenediamine (DMPD) was sublimed three times *in vacuo* to give a colorless solid. An aqueous solution of commercially available *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) dihydrochloride was treated with 28% ammonia. The precipitate obtained was dried and sublimed twice *in vacuo*. *p*-Phenylenediamine-chloranil complex (PPD·CA) was prepared by mixing methylene chloride solu-

tions of PPD and CA at equal molar contents. The complex precipitated was filtered and dried *in vacuo* for about 5 hr at about 45°. Thus the solvent content in the complex was diminished below 5% by weight, as confirmed by elementary analysis. *Anal.* Calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>4</sub>: C, 40.71; H, 2.28; N, 7.91; Cl, 40.06. Found: C, 40.71; H, 2.11; N, 7.79; Cl, 41.20. *N,N'*-Dimethyl-*p*-phenylenediamine-chloranil complex (DMPD<sub>5</sub>·CA<sub>2</sub>) was prepared by mixing benzene solutions of DMPD and CA at equal molar contents. The green precipitate was washed with benzene and ether and dried *in vacuo*, for 2 hr. The composition was found to be DMPD<sub>5</sub>·CA<sub>2</sub>. *Anal.* Calcd for C<sub>32</sub>H<sub>40</sub>N<sub>10</sub>O<sub>4</sub>Cl<sub>8</sub>: C, 53.28; H, 5.16; N, 11.94; Cl, 24.19. Found: C, 52.78; H, 4.94; N, 11.69; Cl, 22.81. *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine-chloranil complex was prepared according to the method described by Eley, *et al.*<sup>9</sup> The result of elementary analysis agreed well with a 1:1 complex. *Anal.* Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Cl<sub>4</sub>: C, 46.86; H, 3.93; N, 6.83; Cl, 34.58. Found: C, 46.69; H, 3.65; N, 6.78; Cl, 34.56. 2,5-Dichloro-3,6-di-*p*-aminoanilino-*p*-benzoquinone was synthesized by dissolving PPD and CA separately in ether (3)-isopropyl alcohol (1) and mixing them at a mole ratio of 2:1.<sup>8</sup> *p*-Benzoquinonediimine and polyazophenylene were synthesized according to the method described in ref 10 and 11, respectively.

**Measurements.** The infrared (ir) spectra were recorded by a Hitachi Perkin-Elmer 225 or a Hitachi EPI-G3 infrared spectrophotometer. A Shimadzu multipurpose recording spectrophotometer MPS-50L was used for the measurements of the electronic absorption spectra. Both ir and uv spectra were measured in all cases in the form of KBr disks.

The materials described above were compressed in a split sphere apparatus developed by one of the present authors.<sup>12</sup> A sphere made of hardened steel was split into six wedge-shaped tapering pistons, the centers of which were all truncated to have square faces making a cubic hollow space. Into this hollow space were placed eight cubic anvils made from cemented tungsten carbide. The innermost corner of each of the eight cubic anvils had a truncated triangular face to enclose an octahedral cavity, into which a pyrophyllite octahedron was placed. The sample was enclosed in the Teflon capsule in the pyrophyllite octahedron. Both the inner and outer anvils were insulated from each other by the insulating cardboard sheets.

The anvil assembly was covered with a pair of hemispherical rubber shells. Then the whole assembly was compressed in a reservoir containing pressure transmitting fluid. The pressure calibration of the cell was performed by measuring the sharp resistance changes at the phase transitions of Bi, ZnTe, Pb, and GaAs and the maximum of the resistance of CdS. Drickamer's new pressure scale was adopted.<sup>13</sup>

## Results

**PPD·CA.** Figure 1 shows the pressure-resistance

(1) R. B. Aust, W. H. Bentley, and H. G. Drickamer, *J. Chem. Phys.*, **41**, 1856 (1964).

(2) R. B. Aust, G. A. Samara, and H. G. Drickamer, *J. Chem. Phys.*, **41**, 2003 (1964).

(3) W. H. Bentley and H. G. Drickamer, *J. Chem. Phys.*, **42**, 1573 (1965).

(4) T. N. Anderson, D. W. Wood, R. C. Livingston, and H. Eyring, *J. Chem. Phys.*, **44**, 1259 (1966).

(5) I. Shirotani, T. Kajiwara, H. Inokuchi, and S. Akimoto, *Bull. Chem. Soc. Jap.*, **42**, 366 (1969).

(6) M. I. Kuhlman and H. G. Drickamer, *J. Amer. Chem. Soc.*, **94**, 8325 (1972).

(7) V. C. Bastron and H. G. Drickamer, *J. Solid State Chem.*, **3**, 550 (1971).

(8) T. Nogami, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **45**, 122 (1972).

(9) D. D. Eley, H. Inokuchi, and M. R. Willis, *Discuss. Faraday Soc.*, **28**, 54 (1959).

(10) R. Willstatter and A. Pfannenstiel, *Chem. Ber.*, **37**, 4605 (1904).

(11) E. Tsuchida, M. Kaneko, and Y. Kurimura, *Makromol. Chem.*, **132**, 209 (1970).

(12) N. Kawai and S. Endo, *Rev. Sci. Instrum.*, **41**, 1178 (1970).

(13) H. G. Drickamer, *Rev. Sci. Instrum.*, **41**, 1667 (1970).

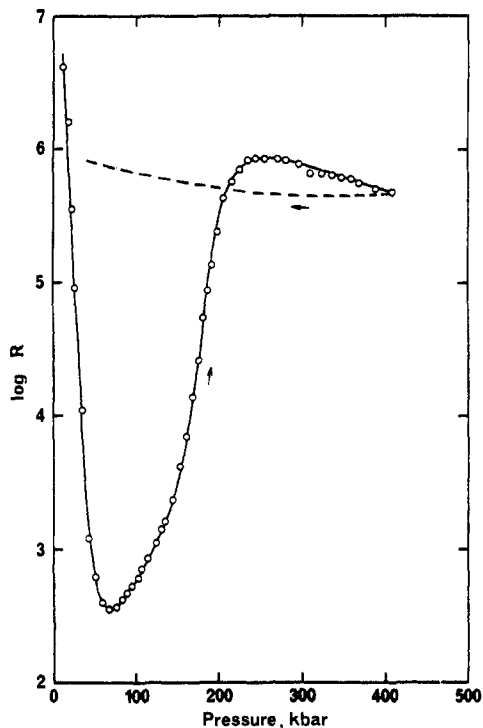


Figure 1. Logarithmic resistance *vs.* pressure for the PPD·CA complex (1:1 complex).

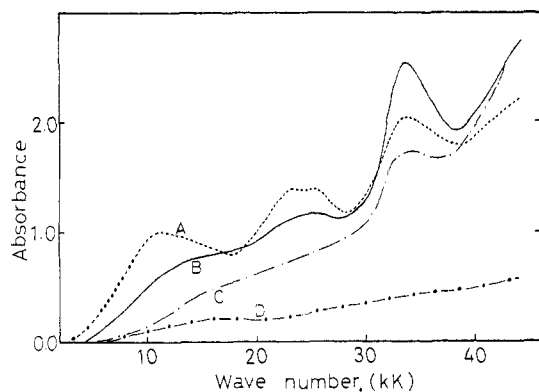


Figure 2. Electronic absorption spectra: A (---) PPD·CA at 1 bar, B (—) the sample recovered after the application of about 200 kbar; C (— · —) the sample recovered after about 240 kbar, D (— · · —) the sample recovered after about 400 kbar. The weight concentrations of the above samples are equal to each other.

curve for PPD·CA. The resistance drops rapidly with pressure until about 70 kbar, then rises up until about 240 kbar, and again decreases slowly at higher pressure. When the pressure is released, the resistance changes as shown by the broken line in Figure 1. Thus, the change of resistance with pressure has been shown to be irreversible, suggesting that some irreversible chemical reactions began to take place at 70 kbar.

Figures 2 and 3 show the electronic and vibrational spectra of the complex recovered after the application of high pressures. The spectra show large changes by the applied pressure. As for the electronic absorption spectra, the bands near 11,000 and 25,000  $\text{cm}^{-1}$  get weaker with pressure, and the band near 33,000  $\text{cm}^{-1}$  gets stronger in the intermediate pressure region and then disappears as shown in Figure 2. In the ir spec-

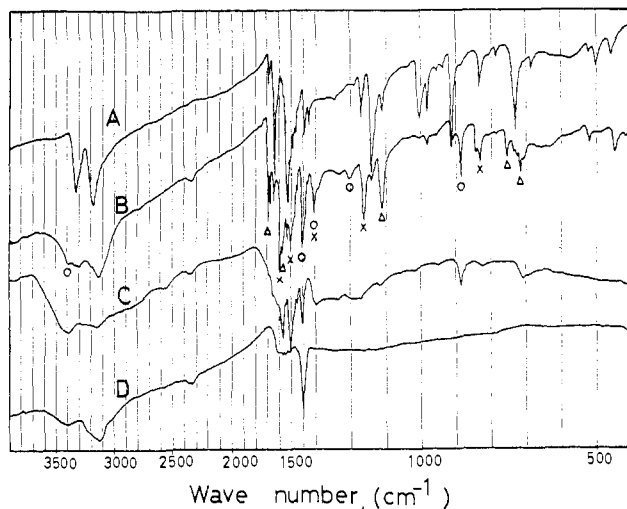


Figure 3. Infrared spectra: (A) PPD·CA at 1 bar, (B) the sample recovered after the application of 200 kbar, (C) the sample recovered after the application of 240 kbar, (D) the sample recovered after the application of 400 kbar.

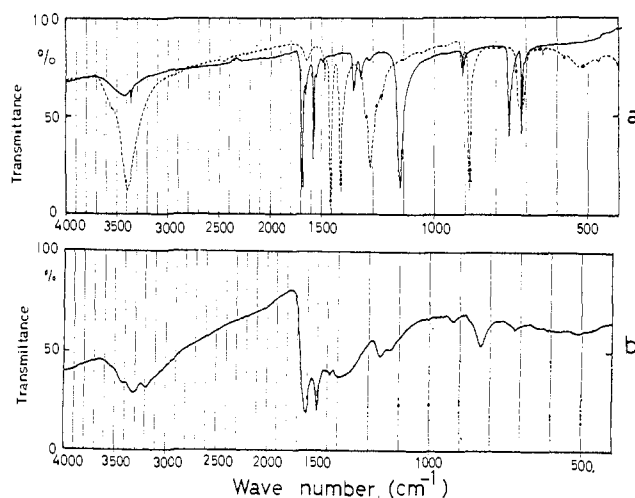


Figure 4. (a) Infrared spectra of chloranil (—) and tetrachloroquinone (---). (b) Infrared spectrum of polyazophenylene.

tra, the absorption bands of PPD·CA become weaker and new bands appear, some agreeing very well with those of CA and tetrachloroquinone (TCHQ). The infrared spectra of CA and TCHQ are shown in Figure 4a by solid and dotted lines, respectively. The bands at 3400, 1410, 1320, 1205, 885, and 720  $\text{cm}^{-1}$ , indicated by circles for the spectrum B in Figure 3, are assigned to TCHQ and those at 1690 (doublet), 1560, 1110, 750, and 710  $\text{cm}^{-1}$ , indicated by triangles in the same figure, to CA. It was also confirmed that the uv absorption spectrum of the ether extract of the recovered sample agrees very well with that of TCHQ. However, in the case where higher pressure is applied, as is shown by C and D in Figure 3, the ir spectra of the recovered samples have no vibrational band of CA and TCHQ, indicating further chemical reactions.

The amounts of  $\text{CA}^-$ ,<sup>14</sup> CA, and TCHQ in the recovered sample were determined from the absorption intensity of the ir bands at 910, 1690, and 885  $\text{cm}^{-1}$ , respectively. When one assumes that no reaction

(14) The ground state of the PPD·CA complex is ionic (see Discussion).

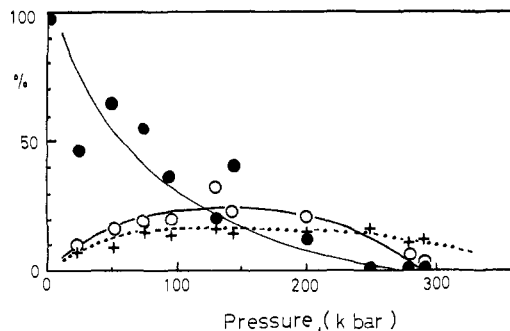


Figure 5. Quantitative yields of  $CA^-$  (●), CA (○), and TCHQ (+) contained in the compressed PPD·CA complexes.

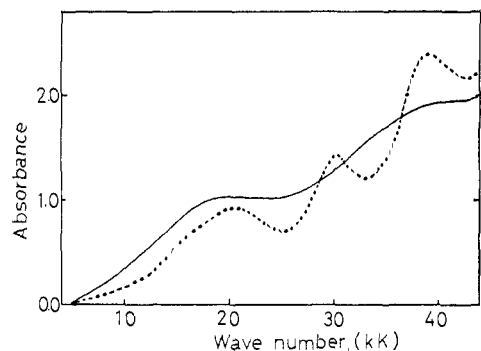


Figure 6. Electronic absorption spectra of 2,5-dichloro-3,6-di-*p*-aminoanilino-*p*-benzoquinone (---) and polyazophenylene (—).

species evaporates from the recovered sample, one can calculate the percentages at which  $CA^-$  has turned into CA or TCHQ. The results obtained are shown in Figure 5. Although CA is formed more than TCHQ in the low-pressure region, the relation is reversed at pressures greater than about 250 kbar. The ir spectra C and D in Figure 3 show more extensive changes compared with B in the same figure. The sum of  $CA^-$ , CA, and TCHQ for samples recovered below 100 kbar is more than 50% of the amount of original CA in the complex, whereas it is less than 20% for those pressed above 300 kbar. These results suggest further reactions proceeding at the high pressure.

The uv absorption spectrum of 2,5-dichloro-3,6-di-*p*-aminoanilino-*p*-benzoquinone which was suspected to be present in the product, with peaks at 20,500, 30,000, and 39,000  $cm^{-1}$ , as is shown in Figure 6, cannot be found in the uv spectra of the high-pressure products of Figure 2. Moreover, the ir spectrum of this compound is different from those of the high-pressure products. *p*-Benzoquinonediimine, also suspected to exist, is colorless and has its electronic absorption at 257 and 265.5 nm in water.<sup>15</sup> No ir absorption band of this compound is found in the spectrum of the high-pressure products. Therefore, these two compounds are excluded from main products under the high pressure.

The electronic and vibrational spectra of polyazophenylene are shown in Figures 6 and 4b, respectively. The ir spectrum of this compound has peaks at 3400, 3320, 3200, 1600, 1500, 1300, 1160, and 830  $cm^{-1}$ . All these bands seem to appear in the spectra of the high-

(15) J. F. Corbett, *J. Chem. Soc. B*, 207 (1969).

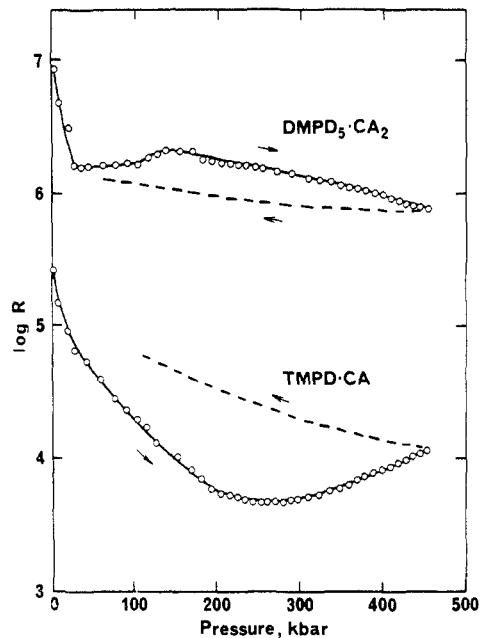


Figure 7. Logarithmic resistance vs. pressure for the  $DMPD_3 \cdot CA_2$  complex and  $TMPD \cdot CA$ .

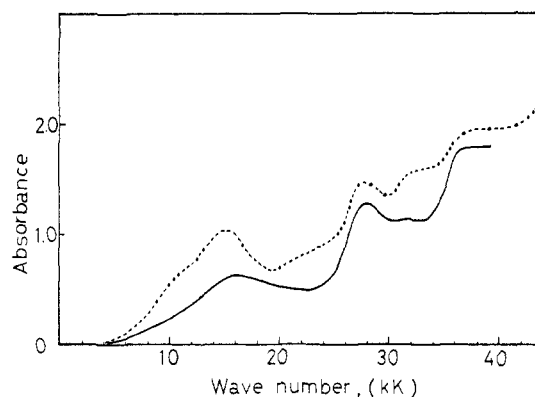


Figure 8. Electronic absorption spectra: (---)  $DMPD_3 \cdot CA_2$  at 1 bar, (—) the sample recovered after the application of about 220 kbar. The weight concentrations of both samples are equal to each other.

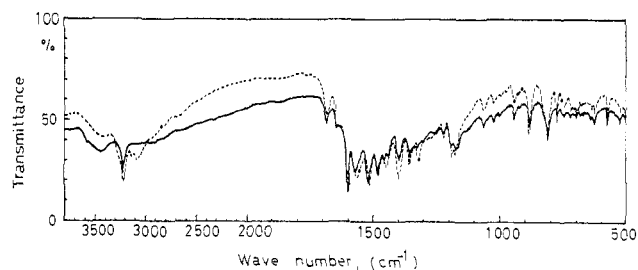


Figure 9. Infrared spectra: (---)  $DMPD_3 \cdot CA_2$  at 1 bar, (—) the sample recovered after the application of 220 kbar.

pressure products, though some of them are not distinct due to overlapping with those of other products and the starting material. They are shown by the signs (X) in the spectrum B of Figure 3. The electronic absorption spectrum of the high-pressure product is rather well accounted for by the superposition of the spectra of CA, TCHQ, PAP, and the remaining starting material. Since PAP has no distinct peak at 33,000  $cm^{-1}$ ,

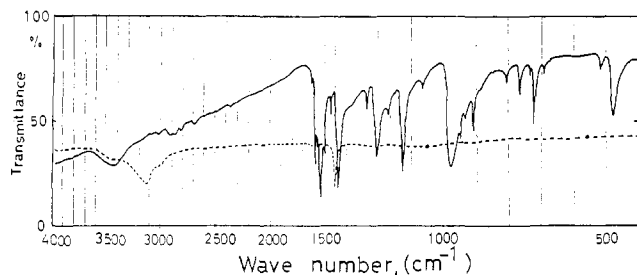


Figure 10. Infrared spectra: (—) TMPD·CA at 1 bar, (---) the sample recovered after the application of 235 kbar.

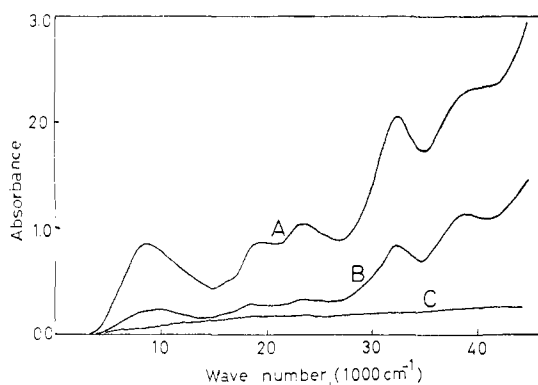


Figure 11. Electronic absorption spectra: (A) TMPD·CA at 1 bar, (B) the sample recovered after the application of 214 kbar, (C) the sample recovered after the application of 235 kbar.

the strong absorption at  $33,000\text{ cm}^{-1}$  in the spectrum B in Figure 2 is explained by the contribution from those of CA ( $34,500\text{ cm}^{-1}$  in *n*-heptane) and TCHQ ( $32,300\text{ cm}^{-1}$  in ether). It is difficult to dissolve PAP in acetone. This coincides with observation for the high-pressure products.

**DMPD<sub>5</sub>·CA<sub>2</sub>.** The resistance of this compound decreases sharply until 40 kbar, then increases gradually, and again decreases at still higher pressure as is shown in Figure 7. Figures 8 and 9 show respectively the electronic and infrared absorption spectra of this compound. The electronic absorption spectra of the recovered sample is considerably different from that of the original material. It was found that this spectral change begins at the pressure of the minimum resistance, and the spectra remain unaltered with application of higher pressures up to 300 kbar.

**TMPD·CA.** The resistance of TMPD·CA decreases until 260 kbar and then increases gradually as shown by Figure 7.<sup>16</sup> All samples pressed in the range from 200 to 300 kbar show the vibrational and electronic spectra with quite few or almost no sharp bands as shown by Figures 10 and 11. These spectra suggest a drastic chemical change at pressures higher than 200 kbar. It is also interesting that these spectra are very similar to those of the products of PPD·CA under extremely high pressures. The attempt to identify reaction products at the intermediate pressure region was not successful. However, the samples recovered after being pressed up to 170~180 kbar, at which the resistance begins to show slight upward shift with time, was found to have the spectral patterns almost the same

(16) This result is very similar to the result by Bentley and Drickamer.<sup>3</sup>

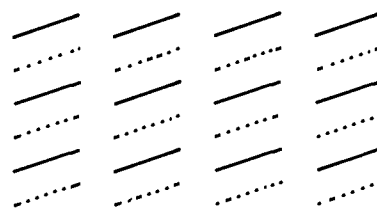


Figure 12. The diagrammatically indicated crystal structure of the PPD<sup>+</sup>CA<sup>-</sup> complex: (—) PPD<sup>+</sup>, (---) CA<sup>-</sup>.

as the original ones with some decreased intensities, as shown in Figure 11.

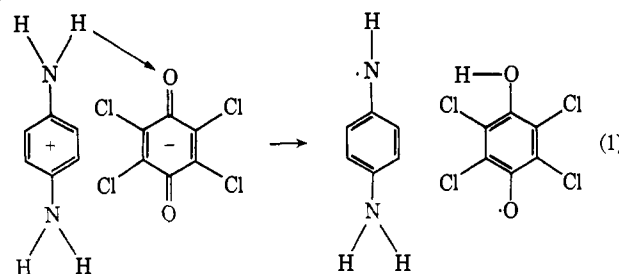
## Discussion

Matsunaga<sup>17,18</sup> found that the ir spectra of some aromatic strong complexes, including PPD·CA and TMPD·CA, are essentially the superposition of the spectra of ion radicals formed from the component molecules. Based on this result, the absorption band near  $25,000\text{ cm}^{-1}$  of our PPD·CA at ordinary pressure can be regarded as the superposition of the local excitation bands of *p*-phenylenediamine cation radical (PPD<sup>+</sup>) and chloranil anion radical (CA<sup>-</sup>), the  $37,000\text{ cm}^{-1}$  band can be assigned to a local excitation band of PPD<sup>+</sup>, and the near infrared band in the region around  $11,000\text{ cm}^{-1}$  can be attributed to the back charge transfer from CA<sup>-</sup> to PPD<sup>+</sup> previously observed in the solid.<sup>19</sup>

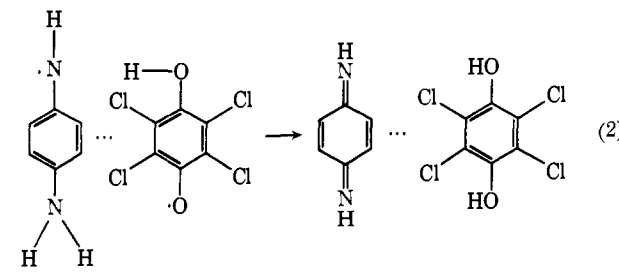
The samples, recovered after application of high pressure, show large change in the electronic spectra, as is seen in Figure 2. Such a change begins to take place already at 70 kbar, where the resistance shows an upward bent and indicates chemical reactions.

The results described in the previous section show that TCHQ, CA, and PAP are formed at high pressure but disappear by further compression. These results can be best accounted for by the following reaction scheme.

(1) Proton transfer between CA<sup>-</sup> and PPD<sup>+</sup> triggered by the compression of the CT complexes, yielding semi-quinone-type radicals.



(2) Further hydrogen transfer reaction between the radicals

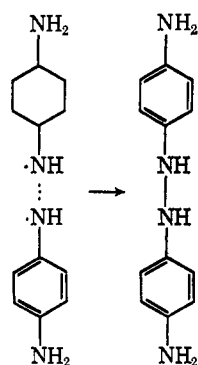


(17) Y. Matsunaga, *J. Chem. Phys.*, **41**, 1609 (1964).

(18) Y. Matsunaga, *Nature (London)*, **205**, 72 (1965).

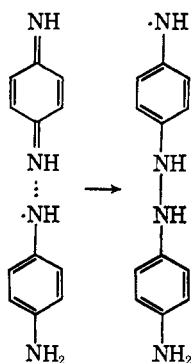
(19) T. Amano, H. Kuroda, and H. Akamatu, *Bull. Chem. Soc. Jap.*, **41**, 83 (1968).

(3) Condensation reaction between PPD semiquinones or *p*-quinodiimines



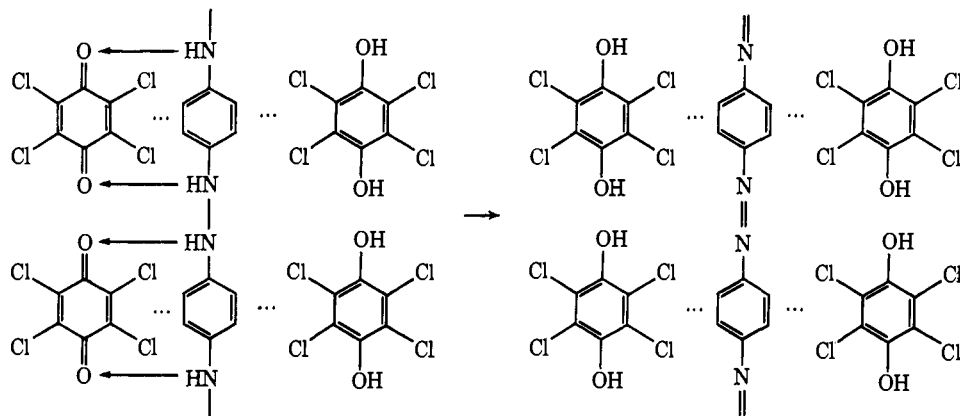
(3)

or



(3')

(4) Further hydrogen transfer reaction from hydrazines to CA, followed by the formation of azo bonding.



(4)

Of course, the above-mentioned scheme is only one of many possible paths. In the crystals, PPD<sup>+</sup> and CA<sup>-</sup> are most probably stacked in such a way as indicated diagrammatically in Figure 12. In view of this, the above-indicated hydrogen transfer and azo-bond formation can occur easily, consecutively between neighboring PPD<sup>+</sup> ions, leading to poly-condensation products of various types with -NH-NH- and -N=N- bonds in the chain. If it is assumed that all nitrogen atoms are linked together by the azo bonds forming a endless chain of PAP and the four hydrogen atoms removed from one PPD are all transferred to the CA molecules, then two hydrogen atoms per one PPD should be in excess, even if all CA molecules are changed into TCHQ. The result that neutral CA molecules are present in the recovered samples tells us either that the PAP chain is rather short or that a considerable number of hydrazine bonds -NH-NH- are present in the PAP chain. The CA observed might be formed by dis-

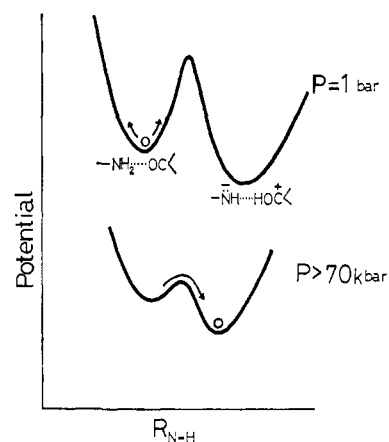
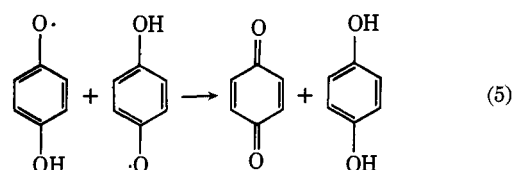


Figure 13. A schematic illustration of proton transfer reaction under high pressure.

proportionations between two semiquinones



(5)

All the above-postulated reactions lead to diminishing of the ionic species such as CA<sup>-</sup> and PPD<sup>+</sup> as manifested by the increase in resistance. This tends to destabilize the ionic ground state of the PPD·CA complex, thus

leading to a partial phase transition in the crystal from the ionic to the nonionic state. The increase in the concentration of neutral CA might be partly due to this transition.

Under very high pressure, the concentrations of CA, TCHQ, and PAP decrease, suggesting further reactions of these species. At present, however, it is difficult to estimate the types of reactions which must take place under these ranges of pressure. One possible type is the condensation reaction between the amino group of PPD and the phenyl group of CA, with the removal of hydrogen chloride.

It has been found that the crystalline PPD·CA complex decomposes gradually by itself at room temperature and atmospheric pressure. The formation of CA and TCHQ was confirmed from the complex kept for about 1 year. This change is thought to occur most probably by proton transfer from PPD<sup>+</sup> to CA<sup>-</sup>, similar to that occurring under high pressure. It is

reasonable that the proton transfer reaction which triggers the subsequent reactions is facilitated by the compression, which must lower the potential barrier for the proton transfer as a result of the shortening of the N...O distances in the complex. This reaction mechanism under high pressure is illustrated schematically in Figure 13.

**DMPD<sub>5</sub>·CA<sub>2</sub>.** Though the changes of the spectra for this compound under high pressures are less than those for PPD·CA as is shown in Figures 8 and 9, it is most likely that some chemical reaction occurs under pressures above 40 kbar. In this case neither CA nor TCHQ is formed. This comparatively inert behavior may arise from the difference in reactivity between DMPD<sup>+</sup> and PPD<sup>+</sup> or from the fact that this compound is not a 1:1 complex as in PPD·CA.

**TMPD·CA.** In this case, the rise in resistance above

200 kbar is not as sharp as in the PPD·CA complex. Neither CA nor TCHQ is formed in this case. From the result of Figures 10 and 11 this complex does not show any intermediate reaction products but leads directly to final spectra as seen in the case of PPD·CA. This may come from the different chemical properties of TMPD<sup>+</sup> which lacks active hydrogen atoms. Its lower reactivity is shown also in the fact that the rise in resistance begins at about 230 kbar and is not as sharp as in the PPD·CA complex, as is seen in Figure 7.

**Acknowledgment.** The authors wish to thank Dr. Yasuaki Okamoto and Professor Shiichiro Teranishi of this university for help in the ir spectral measurement, Mr. Ken-ichi Tanaka for the construction of the high-pressure cells, and Dr. Takashi Nogami of this university for his helpful discussions.

## Emissive Characteristics of Amidic Molecules<sup>1a</sup>

Donald B. Larson, John F. Arnett, Carl J. Seliskar,<sup>1b</sup> and S. P. McGlynn\*

*Contribution from the Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803. Received November 8, 1973*

**Abstract:** Simple amides and various closely related molecules are nonemissive at 77°K. Planar oxamides, however, do phosphoresce and the investigation of oxamidic T<sub>1</sub> states leads to the following conclusions concerning the T<sub>1</sub> state properties of simple amides. (i) The T<sub>1</sub> state is of <sup>3</sup>Γ<sub>ππ\*</sub> type. (ii) This <sup>3</sup>Γ<sub>ππ\*</sub> state is nonemissive. (iii) The energy of this state is 36,000 ≤ E(<sup>3</sup>Γ<sub>ππ\*</sub>) ≤ 38,500 cm<sup>-1</sup>. (iv) The <sup>1</sup>Γ<sub>ππ\*</sub> - <sup>3</sup>Γ<sub>ππ\*</sub> energy separation is ~15,000 cm<sup>-1</sup>. The emissive characteristics of amide-containing molecules (*i.e.*, amides, ureas, oxamides, parabanic acids, acylureas, etc.) are reported and are diverse; this diversity may be rationalized in terms of the following triplet state properties. (v) A T<sub>1</sub> state of <sup>3</sup>Γ<sub>ππ\*</sub> type is nonemissive. (vi) A T<sub>1</sub> state of mixed <sup>3</sup>Γ<sub>nπ\*</sub>/<sup>3</sup>Γ<sub>ππ\*</sub> type is emissive, possesses a weak to moderate intensity output, is usually structureless, and exhibits a decay lifetime of ~10<sup>-2</sup> sec. (vii) A T<sub>1</sub> state of <sup>3</sup>Γ<sub>nπ\*</sub> type is strongly emissive, exhibits vibronic structure involving a dominant C=O stretching mode, and possesses a decay lifetime of ~10<sup>-3</sup> sec. The nature of the T<sub>1</sub> state (*i.e.*, whether <sup>3</sup>Γ<sub>ππ\*</sub>, <sup>3</sup>Γ<sub>nπ\*</sub>/<sup>3</sup>Γ<sub>ππ\*</sub>, or <sup>3</sup>Γ<sub>nπ\*</sub>) is determined by the interactions of an amide group with various other chromophoric groupings including the amide group itself; these interactions may lead to preferential stabilizations of amide <sup>1,3</sup>Γ<sub>nπ\*</sub> or <sup>1,3</sup>Γ<sub>ππ\*</sub> parent states and, hence, to the observed diversity of emissive properties. The energy difference between <sup>1</sup>Γ<sub>ππ\*</sub> and <sup>1</sup>Γ<sub>nπ\*</sub> states is useful in predicting emission behavior for amidic T<sub>1</sub> states. The consequences of these conclusions for the T<sub>1</sub> state of the peptide linkage are discussed.

The importance and prevalence of the peptide bond in biological systems is well known. However, its function in electronic energy-transfer and energy-degradative events is unclear, apparently because the experimental characterization of the lower energy excited states of the peptide linkage has proven to be exceedingly difficult. Some of the lower energy excited electronic states of the singlet manifold are known, at least to the extent of energy, intensity, and, possibly, orbital-excitation nature. In contrast, neither the orbital-excitation nature nor energy of the T<sub>1</sub> state is available.

The deposition of energy in various excited states of the peptide linkage is surely (by virtue of the ubiquity of this unit in the protein and enzyme primary structures) one of the secondary, or even primary, events in radiation biology. Since the peptide T<sub>1</sub> state is one of the

end results of such a deposition, it follows that the nature of this latter state is of some concern.

Our previous attempts<sup>2,3</sup> to characterize the orbital-excitation nature and energy of the T<sub>1</sub> state of the peptide linkage were hampered by a confusing literature about the emissive properties of peptide-related molecules. Our prior approaches were of two types: (1) a survey<sup>2</sup> of the excited electronic state properties of molecules which are isoelectronic with the peptide unit (*i.e.*, O<sub>3</sub>, NO<sub>2</sub><sup>-</sup>, HCOO<sup>-</sup>, HCOOCH<sub>3</sub>, HCONH<sub>2</sub>, etc.) and the devisement of theoretical algorithms which enabled us to interrelate the excited state characteristics of these compounds and to extrapolate them to the peptide linkage; (2) an extensive study of amide-substituted aromatic compounds<sup>3</sup> in which the emissive energies and

(1) (a) Research supported by contract between The United States Atomic Energy Commission-Biology Branch and The Louisiana State University; (b) National Science Foundation Fellow (Fellowship No. 40041).

(2) (a) H. J. Maria, D. B. Larson, M. E. McCarville, and S. P. McGlynn, *Accounts Chem. Res.*, **3**, 368 (1970); ( ) S. P. McGlynn, H. J. Maria, and D. B. Larson, "Organic Scintillators and Liquid Scintillation Counting," D. Horrocks, Ed., Academic Press, New York, N. Y., 1971, p 201.

(3) H. J. Maria and S. P. McGlynn, *J. Chem. Phys.*, **52**, 3399 (1970).