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# Chemical Reactivity of Würster's Salts at Very High Pressure

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The electrical and chemical properties of some Würster's salts have been studied under the static pressure of up to 250 kbar. In most cases the resistances of the salts decreased to the respective minima and then rose irreversively with increasing pressure. Spectral observations on the recovered specimens revealed that such behavior is associated with chemical reaction induced by the pressure. This reaction takes place more readily in the salts of *p*-phenylenediamine cation radical than in those of Würster's red or Würster's blue radicals.

Recent high-pressure studies on organic solid materials have shown that a number of charge transfer complexes[1—5] and ion radical salts[6—9] cause chemical changes above one hundred kilobars[††] or so. The occurrence of chemical reaction is unequivocally indicated by the peculiar behavior in electrical resistance of the specimen showing a minimum on the way of increasing pressure and monotonic rise on the way of decreasing pressure. The samples recovered after the application of pressure were chemically analysed and the reaction mechanisms were elucidated.[2—4]

In a previous paper[4] we reported the pressure-induced chemical reactions in three charge transfer (CT) complexes of *p*-chloranil with aromatic diamines. In the crystalline state of CT complexes the donor and acceptor molecules are generally stacked alternately in columns. The crystals of ion radical salts, on the other hand, are made up of columns of ion radicals. The interactions between adjacent molecules within a column are strong while the interaction between columns are much weaker. Therefore, the chemical reactivities of ion radical salts would be different from those in CT complexes.

The present investigation was undertaken to see chemical reactivity at very high pressure in a series of ion radical salts derived from *p*-phenylenediamine (PD), *N*,*N*-dimethyl-*p*-phenylenediamine and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine The counter ions were iodide, bromide and perchlorate. The electrical resistance measurements of the radical salts were carried out under various pressures and the reaction products recovered after the application of high pressure were analysed spectroscopically.

## Experimental

*Materials.* *p*-Phenylenediamine bromide (PDB) and *p*-phenylenediamine iodide (PDI) were prepared by the reaction of *p*-phenylenediamine with the respective halogens in methanol. Würster's red bromide (WRB) and Würster's red iodide (WRI) were obtained by the reaction of *N*,*N*-dimethyl-*p*-phenylenediamine with the respective halogens in methanol. *p*-Phenylenediamine perchlorate (PDP), Würster's red perchlorate (WRP) and Würster's blue perchlorate (WBP) were prepared by the oxidation of dissolved amine perchlorate and sodium perchlorate with bromine in ethanol.[10] The radical salts were submitted for elementary analyses on formation and were compressed within a week.

*High-pressure System.* The materials described above were compressed in a split sphere-type apparatus.[11] The apparatus is composed of cube, sphere and cylinder, all split up and assembled in a layered structure as shown in Fig. 1. A sphere made of hardened steel is equally divided into six segments, each with a square face at the front. Three out of the six segments are placed in a hemispherical space on the upper part of a cylinder. Similarly, the second assemblage is constructed using the remaining three segments. The two assemblages are set opposed and joined so that a cubic cavity whose ⟨111⟩ direction is parallel to the axis of cylinders is formed in the center of the join.

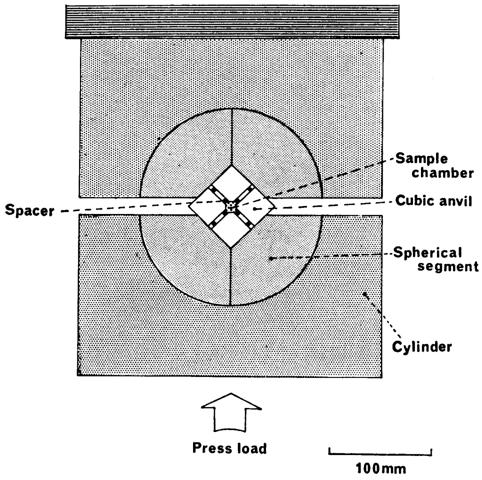

Fig. 1. A schematic drawing of the high-pressure apparatus.

An assemblage of eight cubic anvils made of cemented tungsten carbide is placed in the cubic cavity. A corner of each cubic anvil is truncated to form a triangular face. When the eight cubic anvils are put together an octahedral hollow space is formed in the center of the assemblage. Into this space is placed an octahedral pressure-transmitting medium made of pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$). Crushable spacers made of cardboard are sandwiched in the gaps among the eight cubic anvils. When the two cylinders containing a split sphere and cubes are compressed in a uniaxial press, the thickness of the spacers decreases and quasi-hydrostatic high pressure is generated in the octahedral chamber. The pressures are calibrated by measuring the sharp resistance changes at the phase transitions of Bi ($\mathrm{Bi}_{\mathrm{I-II}}$ at 25 kbar, $\mathrm{Bi}_{\mathrm{V-VI}}$ at 74 kbar), ZnTe (127 kbar), Pb (132 kbar), ZnS (153 kbar), GaAs (177 kbar) and GaP (222 kbar).[12—16]

As shown in Fig. 2 the sample is enclosed within a Teflon capsule which is inserted into a hole drilled from a face to face of the ocatahedral chamber. Two platinum electrodes

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†† 1 bar=$10^5$ Pa.

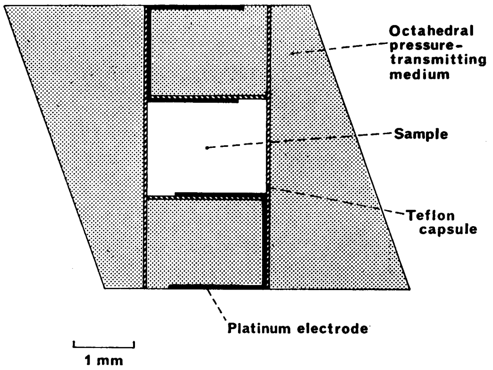

Fig. 2. A cross section of the octahedral pressure chamber.

for resistance measurements are taken out of the octahedron and are in contact with the top faces of the two of the eight cubic anvils. Electrical insulation between the anvils is provided by cardboard spacers and also by thin sheets of mica.

*Measurements.* The electrical resistance of the samples under pressure is measured *via* two cubic anvils with a Keithley 160B digital multimeter. The resistance of the cubic anvils is low enough to be neglected. On the other hand, the resistance of the pressure-transmitting medium is higher than that of any of the present samples by more than one order of magnitude. Thus the observed resistance reflects substantially the behavior of the sample. For the recovered samples after the application of pressure, the electronic spectra are obtained on the KBr disks with a Shimadzu Model MPS-50L multipurpose spectrometer. The vibrational spectra are obtained on a JASCO JRA-1 type diffraction grating infrared spectrometer using a similar KBr method.

## Results

*PD Cation Radical Salts.* In Fig. 3 the electrical resistance of PDP is plotted on a logarithmic scale as a function of pressure. The resistance drops rapidly with pressure up to about 130 kbar. At higher pressure the resistance begins to rise. A noticeable upward drift of the resistance continues while the pressure is kept fixed. Beyond 200 kbar the resistance begins to decrease slowly. The resistance changes on the unloading process as shown by a dotted line in the diagram.

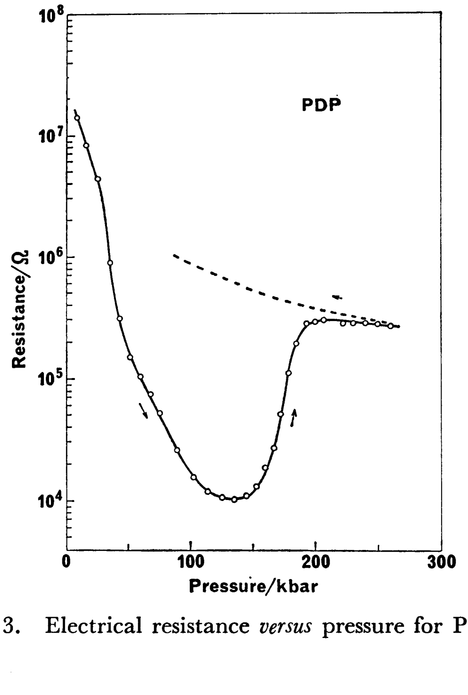

Fig. 3. Electrical resistance *versus* pressure for PDP.

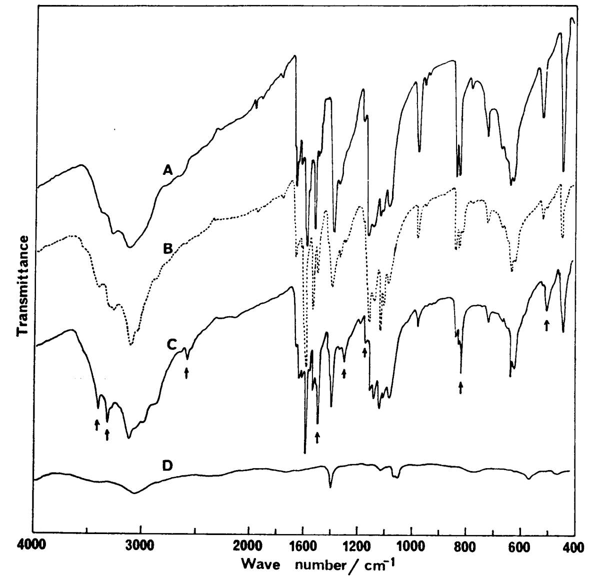

Fig. 4. Infrared spectra.
A: PDP at 1 bar, B: the sample recovered after the application of 140 kbar, C: the sample recovered after the application of 180 kbar, D: the sample recovered after the application of 220 kbar.

Figure 4 shows the infrared (IR) spectra of PDP before and after the compression. It should be noted that there was no appreciable change in the spectrum for the specimen compressed to pressures lower than 130 kbar, where a minimum appears in the electrical resistance. At 140 kbar new bands become to appear on the IR spectrum B, and at 180 kbar they become stronger as shown by the spectrum C. The bands indicated by arrows in Fig. 4, at 3420, 3330, 2590, 1505, 1300, 1195, 820, and 505 $\mathrm{cm}^{-1}$, are assigned to 4-aminophenylammonium perchlorate, $[\mathrm{PDH}^+][\mathrm{ClO}_4^-]$. This was confirmed by the comparison of the bands with those in the IR spectrum of the synthesized authentic sample. The spectrum D is quite simple, suggesting that the product at higher pressure is polymeric. In the spectra of the high-pressure products in Fig. 4, there remain the bands responsible for the starting material, showing that the reaction in this system is rather slow.

Figure 5 shows the electronic absorption spectra of PDP and its reaction products recovered after the application of pressure, all specimens containing equal amounts of PDP in each of the KBr pellets. In the spectrum of PDP at 1 bar, the band at 13000 $\mathrm{cm}^{-1}$ is assigned to the charge transfer between cation radicals, whereas the peaks at 28800 and 35500 $\mathrm{cm}^{-1}$ are due to the local excitation between cation radicals.[17] As seen in Fig. 5 the band at 13000 $\mathrm{cm}^{-1}$ becomes weaker and shifts to blue with increasing pressure. The intensities of the peaks at 28800 and 35500 $\mathrm{cm}^{-1}$ decrease and the peaks shift to red with increasing pressure. The spectrum

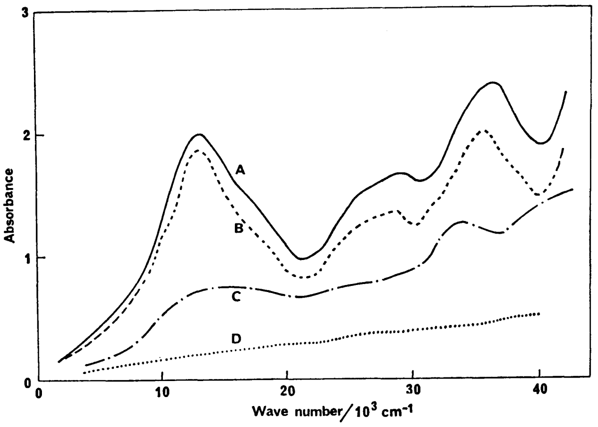

Fig. 5. Electronic absorption spectra.
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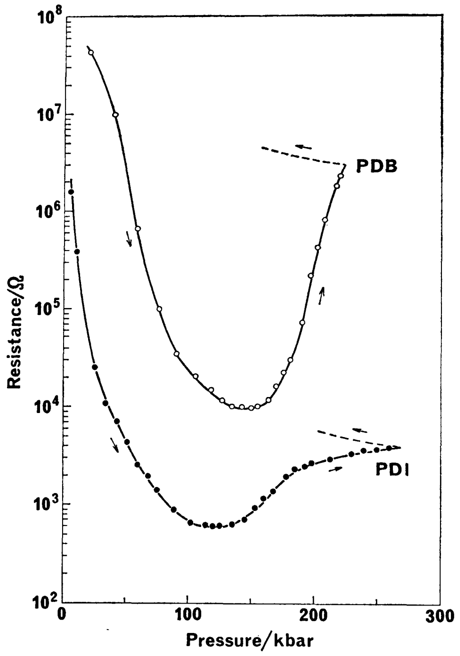


Fig. 6. Electrical resistance *versus* pressure for PDB and PDI.

C in Fig. 5 is well accounted for by a formation of $[PDH^+][ClO_4^-]$. In coincidence with the IR spectrum D in Fig. 4, the spectrum D in Fig. 5 is quite simple.

Figure 6 shows the electrical resistance *versus* pressure curves for PDB and PDI. The resistance of PDI is lower than that of PDB by about one order of magnitude throughout the pressure range covered. The resistance of PDB decreases by approximately four orders of magnitude when pressurized to 150 kbar, where a minimum appears. Above this pressure the electrical resistance of PDB begins to increase. As the pressure is released the resistance increases monotonously, suggesting that chemical reaction takes place in PDB above 150 kbar. The electrical resistance of PDI decreases by compression to about 120 kbar, above which it begins to rise. The behavior is irreversible on unloading process. This again suggests that chemical reaction takes place. The recovered PDI specimens were inspected after the application of pressures up to 200 kbar. Both the IR and electronic absorption spectra of compressed PDI were quite similar to those of compressed PDP. This shows that the high-pressure product of PDI is $[PDH^+][I^-]$.

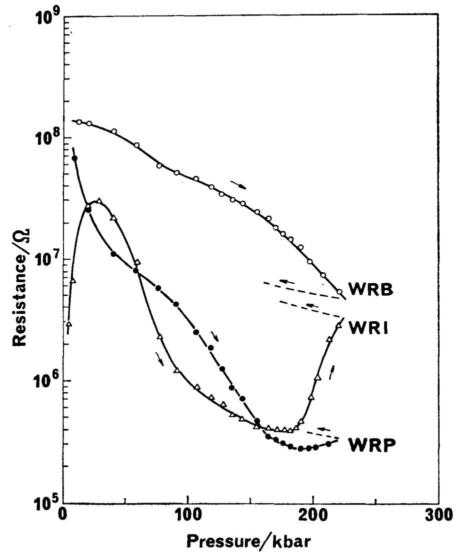


Fig. 7. Electrical resistance *versus* pressure for WRP, WRB, and WRI.

*WR Cation Radical Salts.* Figure 7 shows the electrical resistance of WRP, WRB, and WRI as a function of pressure. The resistance of these WR radical salts at high pressure are higher than those of PD radical salts. For WRP there appears a broad minimum around 190 kbar. The electrical resistance of WRP changes on unloading process in a different way from that shown on compression, indicating chemical reaction. The resistance of WRB decreases monotonously up to the highest pressure applied in this work. There might be a minimum in resistance at higher pressure. The resistance of WRI first increases to about 40 kbar, then decreases and after a broad minimum it increases again. The first increase of resistance is not well understood at present. From the resistance-pressure curve, the solid-state reaction in WRI seems to take place at a pressure of 180 kbar. No attempt was made to recover the specimen after the application of pressure and to carry out its spectral inspection.

*WB Cation Radical Salt.* Figure 8 shows the change of electrical resistance of WBP as a function of pressure. There appear two minima, the first at about 25 kbar, and the second around 220 kbar. WBP transforms at ambient pressure from the orthorhombic to monoclinic structure near 190 K. The pressure dependence of this transition temperature is reported to be 10 deg/kbar.[18] The linear extrapolation to room temperature locates the transition pressure at about 11 kbar, which is much less than the first minimum pressure. It is not certain whether or not the first

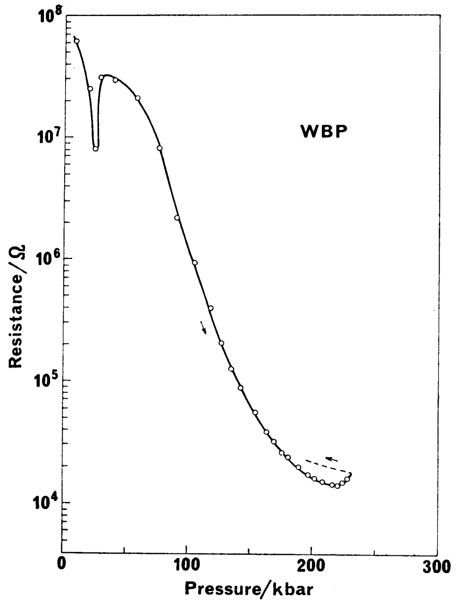


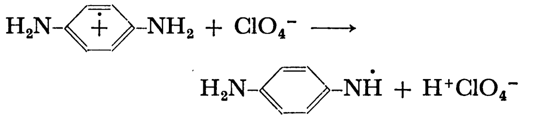
Fig. 8. Electrical resistance *versus* pressure for WBP.

minimum reflects the phase transition. Since the resistance drifts upward after the second minimum and increases irreversibly on decreasing pressure, the second minimum is attributable to chemical reaction, as in the case of PD radical salts, WRP and WRI.

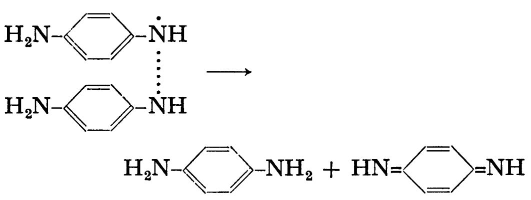
## Discussion

The product of the high-pressure reaction in PDP is, as described earlier, $[PDH^+][ClO_4^-]$. A possible scheme for the reaction to $[PDH^+][ClO_4^-]$ from PDP is as follows.

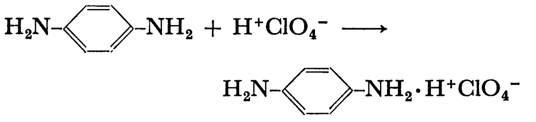
i) Proton transfer between $ClO_4^-$ and PD cation radicals, yielding semi-quinone type radical and $HClO_4$.



ii) Disproportionation between two radicals to form neutral PD and *p*-benzoquinone diimine.



iii) Addition of $HClO_4$ to PD.



When PDP crystal is heated at 120 °C under vacuum, a solid-state reaction takes place within several hours. The products are PD, 4,4′-diaminoazobenzene (AZ), $N^1,N^4$-bis(*p*-aminophenyl)-2,5-diamino-1,4-benzoquinone diimine (Bandrowski's base, BB) and its polymer, among which BB-polymer and PD are predominant.19) These materials are not recognized in the spectra of the high-pressure product of PDP. In order that BB20) be produced by the linkage of three adjacent PD molecules in the crystalline state, the PD molecule to be centered should rotate to a certain amount because they are stacked in parallel face to face positions. This rotation will be facilitated in solids at higher temperature in vacuo, while it will be rather retarded under high pressure. BB is also synthesized by the reaction of PD cation radical with the parent molecule in ethanol solution.21) The requisite linkage of three molecules for the formation of BB would be much easier in the solution than in the solid state.

Table 1. Pressure at which a minimum appears in the electrical resistance of respective Würster's salts

| Cation radical | Counter ion | | |
|---|---|---|---|
| | $ClO_4^-$ | $Br^-$ | $I^-$ |
| | | $P_{min}$/kbar | |
| $PD^+$ | 130 | 150 | 120 |
| $WR^+$ | 190 | >230 | 180 |
| $WB^+$ | 25<br>220 | a) | a) |

a) Not measured.

Table 1 lists $P_{min}$, the pressure at which the electrical resistance shows minimum. As described earlier, $P_{min}$ reflects the commencement of solid-state reaction. In PD radical salts $P_{min}$ increases with the order; iodide, perchlorate and bromide. The reactivity19) of the PD radical salt in the thermal reaction at ambient pressure becomes lower in the same sequence, indicating that the chemical reactivity in PD radical salts at high pressure is similar to the thermal reaction at 1 bar, although the products and hence the mechanisms are different. In the WR radical salts, the chemical reactivity at high pressure decreases with the order; WRI, WRP and WRB, in coincidence with the salts of PD radical. The counter ions are, therefore, very effective in the chemical reactivity in PD and WR radical salts at high pressure.

For PDP, WRP, and WBP, on the other hand, the chemical reactivity decreases at high pressure as the cation radical changes in the order PD, WR, and WB. The order holds also for salts of bromide and iodide. This sequence of chemical reactivity may be attributed to the difference in the number of active protons in PD, WR, and WB molecules, respectively.

In some of the present radical salts the interplanar spacing of cation radicals is quite short with respect to that calculated from the van der Waals distances. The separation is 3.105 Å in WRB22) and 3.550 Å in WBP,23) respectively, which is to be compared with that of tetrathiafulvalenium (TTF) cation radical in TTF salts. The spacing of TTF molecules is 3.57 Å in $TTFBr_{0.8}$,24) 3.56 Å in $TTF_7I_5$25) and 3.48 Å in TTF-TCNQ (tetracyanoquinodimethane),26) respectively. These TTF cation radical salts undergo chemical reactions at pressures below 50 kbar,8,9) whilst much higher pressures are required for the reactions in Würster's salts. Therefore, the short spacing of the cation radicals does not necessarily facilitate the chemical reactivity of the compressed radical salts. Partial charge transfer, prevailing in the TTF cation radical salts,[24,27] seems to be more effective in causing the chemical changes at high pressure. This is evidenced by the pressure-induced chemical reaction of TCNQ anion radical salts[7-9] in which is also observed partial charge transfer.

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