EFFECT OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF ORGANIC SUBSTANCES

II   α, α'-Diphenyl-β-Picryl Hydrazyl

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The electrical conductivity of α, α'-diphenyl-β-picryl hydrazyl has been measured at temperatures of 15°~100°C, at pressures up to 70 kb by the use of a compact cubic type anvil apparatus. A resistivity reduction as high as two orders of magnitude was observed between 30~70 kb at room temperature. The resistivity decreases with increasing temperature at constant pressure. The resistivity under pressure follows the usual exponential law; $\rho = 1/\sigma = \rho_0 \exp(E/kT)$. The activation energy also decreases with increasing pressure. The effect of pressure on the conduction is discussed.

Introduction

Many organic compounds, especially those with mobile π-electrons, show appreciable electrical conductivity, but little has been published on the effect of pressure on the electrical properties. This behavior seems to be closely associated with the amount of π-electron overlap between adjacent molecules or intermolecular distance.

The organic solid free radical, α, α'-diphenyl-β-picryl hydrazyl (DPPH) behaves as a semiconductor[1] with considerably low activation energy of 0.13 eV.[2] However, the value of recent measurement for single crystal is 0.75~0.8 eV[3] or 0.6 eV.[4] The role of odd electron in the conduction process in crystals of the substances having radical character is less well understood. The molecular compounds that are so conducting are in some cases paramagnetic, e. g., pyrolyzed polyacrylonitrile[5] whose conductivity has been measured under high pressure in the previous paper.[6] The conductivity of DPPH as a function of pressure has been reported at room temperature.[7]

The present paper describes the temperature dependence of resistivity on DPPH under high pressure. The comparison has been made with the results of pyrolyzed polyacrylonitrile. It is one

1) D. D. Eley and M. R. Willis, "Symposium on Electrical Conductivity in Organic Solids", Interscience, New York (1961) p. 257
2) D. D. Eley and G. D. Parfitt, *Trans. Faraday Soc.*, **51**, 1529 (1955)
3) H. Inokuchi, Y. Harada and Y. Maruyama, *Bull. Chem. Soc. Japan*, **35**, 1559 (1962)
4) K. Masuda and J. Yamaguchi, *J. Phys. Soc. Japan*, **20**, 359 (1965)
5) A. V. Topchiev, M. A. Geiderikh, B. E. Davydov, V. A. Kargin, B. A. Brentzel, I. M. Kystanovich and L. S. Polack, *Dokl. Akad. Nauk S.S.S.R.*, **128**, 312 (1959)
6) J. Osugi and K. Hara, *This Journal*, **36**, 20 (1966)
7) H. Inokuchi, I. Shirotani and S. Minomura, *Bull. Chem. Soc. Japan*, **37**, 1234 (1964)

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of the features of the present experiment that high pressures have been generated by the use of a cubic type anvil apparatus. Most of the previous works were made by an opposed anvil apparatus. This work has been carried out on polycrystalline samples, owing to the difficulties encountered in obtaining single crystals of sufficient size. The results of the comparison of ac values with dc values at high pressure[8] proved that the effect of intergranular boundary is virtually negligible at pressure more than 25 kb.

Experimentals

The α, α'-diphenyl-β-picryl hydrazyl examined was prepared by purification of the substance obtained from Nakarai Chemical Co., Ltd. The possible mixed substance, α, α'-diphenyl-β-picryl hydrazine (DPPHn) was removed by the oxidation[9] with lead dioxide and anhydrous sodium sulfate. The dark violet crystal was grown from the carbon disulfide solution. This substance was identified by both infrared and ultraviolet spectra, which are shown in Fig. 1 (A), (B). The chemical formula of DPPH is as follows.
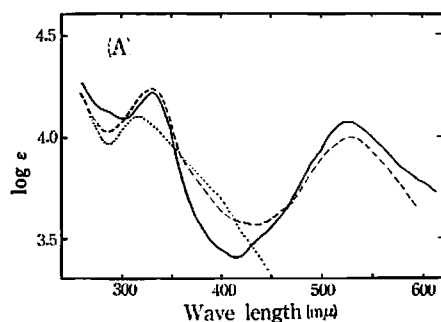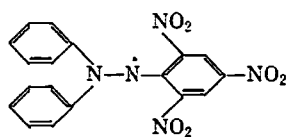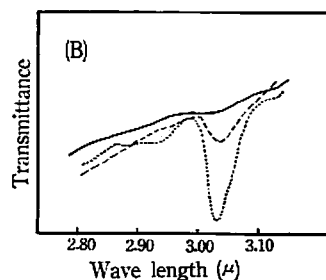

Fig. 1   (A) Visible and ultraviolet absorption spectra
(B) Infrared absorption spectra (NH region)
————: Purified DPPH
— — —: Commercial DPPH
············: DPPHn

8) R. S. Bradley, J. D. Grace and D. C. Munro, *J. Phys. Chem. Solids*, **25**, 725 (1964)
9) R. H. Poirier, E. J. Kahler and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952)

The electrical resistivity measurement was made under high pressure in a compact cubic type anvil apparatus, whose pressure calibration techniques and heating methods had been described in detail.[9)10)] The sample, precompressed into a cylindrical pellet of 4 mm diameter and about 1 mm thickness, was placed in a pyrophyllite insulating sleeve, outside of which two cylindrical graphite heaters were situated. We can get a well-defined stable temperature. A schematic view of the internal structure of the pyrophyllite cube for the resistivity measurement is shown in Fig. 2. For room temperature experiments the sleeve of silver chloride was used in order to get a more hydrostatic condition. The temperature range was $15° \sim 100°C$. Resistivity was measured by means of a VTVM electrometer.
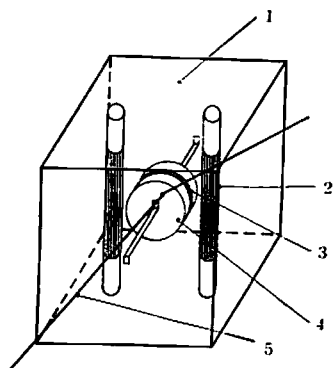

Fig. 2   Schematic view of a pyrophyllite sample cube for resistance measurement
1: Pyrophyllite,   2: Carbon heater,   3: Specimen,
4: Electrode,   5: Thermocouple

Results and Discussion

The pressure dependences of the electrical resistances were measured under constant temperature. The highest pressure applied was 70 kb. There is a hysteresis between ascending and descending pressures, which arises largely from the friction in the sample holder. After releasing pressure, the resistivity is the same as before. Fig. 3 shows the result at room temperature. The resistivity at 30 kb is $7.5 \times 10^6 \, \Omega \cdot$cm, and $8.0 \times 10^4 \, \Omega \cdot$cm at 70 kb. The change is of the order of two powers of ten between 30 kb and 70 kb. The sample was examined by means of an infrared spectrometer before and after the measurements. These infrared spectra were found to be exactly superimposable. There was no indication of chemical change in the pressure and temperature range of this work. Above 150°C, however, a small but detectable change had occurred in the infrared spectrum.

The typical data of resistivity *versus* pressure at various temperatures are shown in Fig. 4. The data reported here were the average values of several runs on different samples of the freshly recrystallized material.

As shown in Figs. 3 and 4, the resistivity decreases rapidly in the lower pressure region, and gradually the rate of decrease becomes slow as pressure increases. This seems to be qualitatively ascribed to higher compressibility in the former and lower compressibility in the latter. The com-

10)   J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)

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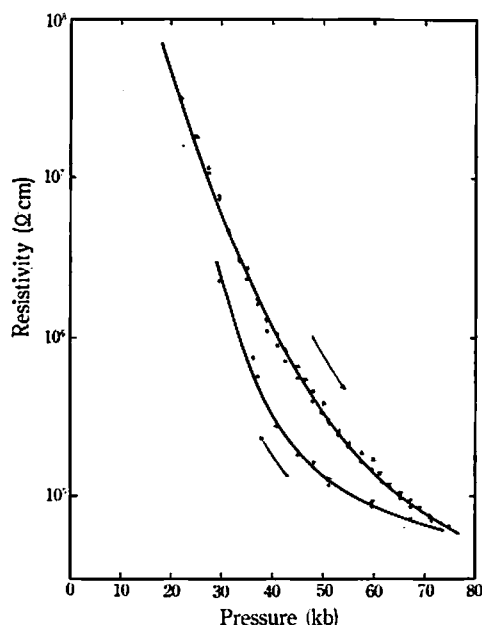

Fig. 3   Effect of pressure on resistivity of DPPH
         at room temperature. The dots and crosses
         refer to two different runs.
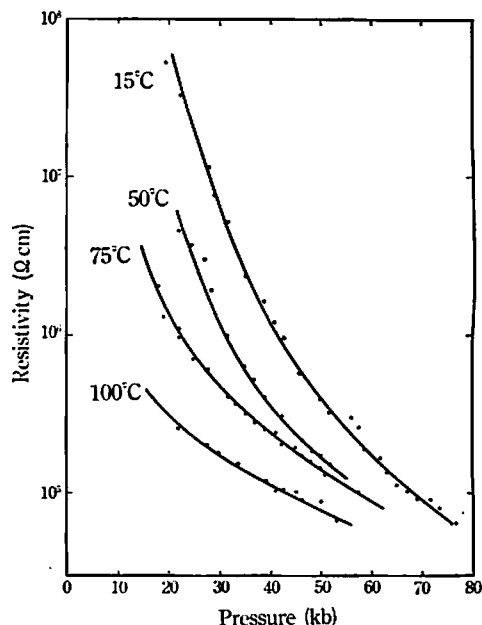
Fig. 4   Effect of pressure on resistivity of DPPH
         at 15°, 50°, 75°, and 100°C

pressibility of DPPH is not available. Bridgman's results for several aromatic compounds[11] indicate that they have compressibilities which are very much alike. Since these data cannot be obtained only up to 25 kb, they are extrapolated to 80 kb along the corresponding curve of sulfur[12] which has the analogous pressure-volume data to the above compounds. This is illustrated in Fig. 5. One can see that the compressibilities are decreasing markedly with pressure. Fig. 6 shows the replots of log resistivity of DPPH *versus* fractional volume change. The corresponding plots for the results of PAN[*] are shown
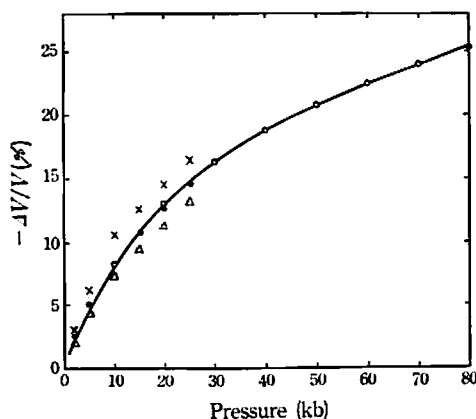

Fig. 5   Change in volume of molecular crystals with
         pressure
         (●) Anthracene   (✕) Naphthalene
         (△) Anthraquinone   (○) Sulfur

11)   P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **76**, 9 (1945)
12)   P. W. Bridgman, *ibid.*, **76**, 1 (1945)
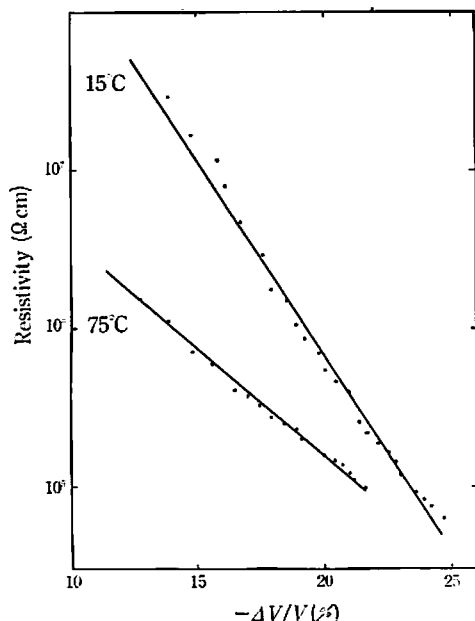 *)   Polyacrylonitrile

Fig. 6   Relationship between resistivity and
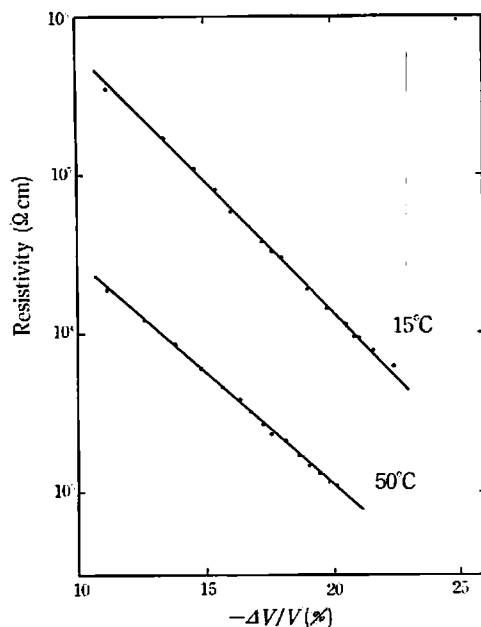relative volume change of DPPH

Fig. 7   Relationship between resistivity and
relative volume change of PAN

in Fig. 7. Both give nearly linear relationship over this pressure range, though the compressibility data are not exact. These results are similar to those obtained for some fused-ring aromatic compounds by Samara and Drickamer.[13] Due to weak binding, organic solids should be quite compressible, especially in the low pressure region. Under high pressure the molecules are brought closer, and this leads to a larger orbital overlap between adjacent molecules.

The conductivity can be expressed as

$$\sigma = \frac{1}{\rho} = e\mu n,\qquad(1)$$

where n is the carrier concentration and μ is the mobility, or, assuming the exponential temperature dependence to originate solely from n,

$$\sigma = e\mu n_0 \exp(-E/kT),\qquad(2)$$

where E is the thermal activation energy for conduction and n_0 the effective number of the charge carrier.

Fig. 8 shows electronic resistivity, which decreases exponentially with the reciprocal of the absolute temperature. This implies that equation (2) is also applicable under high pressure. The slope gives the activation energy for conduction at each pressure, the value of which tends to decrease with increasing pressure as shown in Table 1. Recently, Shirotani, Inokuchi, and Minomura[14] have reported to be 0.11 eV under the pressure of 127 kb by the use of a Drickamer type cell. The

13) G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 474 (1962)

14) I. Shirotani, H. Inokuchi and S. Minomura, *Bull. Chem. Soc. Japan*, **39**, 386 (1966)
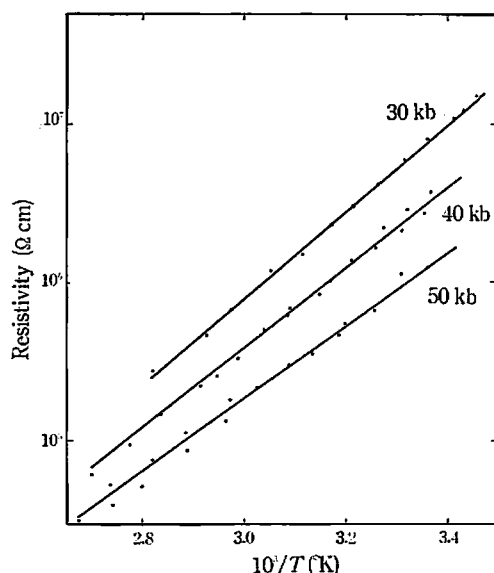
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Fig. 8 Relationship between resistivity and temperature at 30, 40, and 50 kb

value seems to decrease further with increasing pressure more than 50 kb, though there are some difficulties in the direct comparison, *e.g.* the difference of hydrostatic condition. Eley *et al.*'s value at atmospheric pressure, 0.13 eV is found to be too low, compared with the values under high pressure. On the other hand, the value 0.75~0.8 eV or 0.6 eV is somewhat large, but this seems to be the case. The activation energy may decrease remarkably in the first 30 kb. But it may not be possible to compare this value directly with the other, since DPPH has been reported to have several types of crystal structure,[15] which may affect its electrical properties.

Table 1 Activation energies and estimated mobilities under various pressures at room temperature

Substance	Pressure (kb)	Activation energy (eV)	Estimated mobility (cm^2/V·sec)
DPPH	30	0.24	1.0×10^{-5}
	40	0.21	2.2×10^{-5}
	50	0.19	5.0×10^{-5}
PAN	20	0.36	3.7×10^{-2}
	30	0.32	3.2×10^{-2}
	40	0.30	3.7×10^{-2}
	50	0.27	2.9×10^{-2}
Phthalocyanine	12.5	0.44	1.7×10^{-2}
	50	0.34	3.4×10^{-2}
Cu-Phthalocyanine	12.5	0.49	3.7×10^{-3}
	50	0.43	7.4×10^{-3}

15) D. E. Williams, *J. Chem. Soc.*, 1965, 7534

The values of the product μn_0 can be calculated from the published data of E and σ at atmospheric pressure for each substance. The figures thus obtained were found to range from 10^9 to 10^{32}. But, for the clear understanding of the conducting mechanism, the two quantities must be separated. Many, Harnik, and Gerlich[16] made an attempt to separate the quantities, by assuming the order of magnitude n_0. The upper limit was estimated to be of the order of 10^{23} from a "free molecular model". In crystals with strong binding, such as germanium, n_0 is about 10^{20}. As the binding in molecular crystal is weak, the lower limit can be reasonably taken to be of the order of 10^{20}.

From the above assumptions we can estimate the mobility at each pressure. Table 1 also contains the estimated mobilities of DPPH thus obtained at various pressures. For comparison, those of PAN, Phthalocyanine,[17] and Cu-Phthalocyanine[17] are also listed. n_0 was taken as 10^{21}. We can see that the estimated mobility of DPPH tends to increase slightly with pressure. Phthalocyanine and Cu-Phthalocyanine have the same tendency and the amount of increase is nearly the same, while that of PAN does not change. But in all substances the amount of change in the mobility can be considered to be small, compared with the amount of the change of resisitivity with pressure.

Thus the change of conductivity with pressure mainly comes from the change of the activation energy for conduction. Moreover, the activation energy depends on the intermolecular distance.

The above discussion suggests the need for independent measurement of mobility under high pressure.

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16) A.Many, E. Harnik and D. Gerlich, *J. Chem. Phys.*, **23**, 1733 (1955)
17) R. S. Bradley, J. D. Grace and D. C. Munro, *Trans. Faraday Soc.*, **58**, 776 (1962)