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Electrical Properties of Some Charge-Transfer Complexes under High Pressure

T. N. ANDERSEN, D. W. WOOD,* R. C. LIVINGSTON, AND H. EYRING
Rate Processes Institute, University of Utah, Salt Lake City, Utah

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The electrical resistances of several polyaromatic–halogen intermolecular charge complexes (pyrene with varying concentrations of bromine, coronene with iodine, and perylene with bromine) were measured at pressures up to 80 kbar. Activation energies as a function of composition were measured for the pyrene·XBr_2 samples, as were Seebeck coefficients and activation energies at varying pressures for one of the complexes. The resistance decrease with increasing pressure is interpreted as due to an increase in concentration of charge carriers. Possible states in which the charge carriers exist are discussed.

INTRODUCTION

THE effect of high pressure on the electrical resistance, thermal-activation energy, and Seebeck coefficient of several aromatic–halogen intermolecular charge complexes has been studied. Most previous electrical studies on intermolecular charge complexes have been made at or near atomspheric pressure,[1–6] although two recent works have measured resistances of several complexes up to several hundred kbar.[7,8] The latter investigators found at first a general lowering of resistance as pressure was increased and for several charge-transfer complexes found a minimum in the resistance at higher pressures. The materials here investigated were eight pyrene bromine mixtures, pyrene·XBr_2, with X having the values 0.15, 0.30, 0.35, 0.55, 1.25, 1.80, 2.25, and 3.80. Equal molar mixtures of perylene with bromine and coronene with iodine were also studied.

The bromine complexes were prepared by Zinke's method[9] in which the aromatic solid was placed in an atmosphere of bromine for various lengths of time (6 to 192 h at room temperature for the pyrene·XBr_2 complexes). The iodine complex was prepared by adding iodine to a benzene solution of the aromatic.[10] After the reaction, the samples were vacuum desiccated in order to remove excess halogen, and were then weighed in order to determine the amount of total halogen introduced. Complex formation is recognized by the change from light (polyaromatic) to dark color, as well as by mass increase. It was found that very little weight loss ($<1\%$) occurred in a stoppered bottle after vacuum desiccation; thus the composition of the product did not change significantly after the initial

* Present address: E. I. DuPont de Nemours and Company, Wilmington 98, Delaware.

[1] H. Akamatu, H. Inokuchi, and Y. Matsunaga, Bull. Chem. Soc. Japan **29,** 213 (1956).

[2] H. Akamatu, H. Inokuchi, and Y. Matsunaga, Nature **175,** 168 (1954).

[3] R. Sehr, M. M. Labes, M. Bose, H. Ur, and F. Wilhelm, *Symposium on Electrical Conductivity in Organic Solids,* edited by H. Kallman and M. Silver (Interscience Publishers, Inc., New York, 1961), p. 309.

[4] J. Kommandeur and L. S. Singer, *Symposium on Electrical Conductivity in Organic Solids,* edited by H. Kallman and M. Silver (Interscience Publishers, Inc., New York, 1961), p. 325.

[5] J. Kommandeur and J. R. Hall, J. Chem. Phys. **34,** 129 (1961).

[6] L. S. Singer and J. Kommandeur, J. Chem. Phys. **34,** 133 (1961).

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

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

[9] A. Zinke and A. Pongratz, Ber. **69,** 1591 (1937); **70,** 214 (1937).

[10] K. Brass and E. Clar, Ber. **65,** 1660 (1932).

weighing. This indicates the absence of reactions[11] such as $C_6H_6+Br_2 \rightarrow C_6H_5Br+HBr$. Nevertheless, the experiments were performed on freshly prepared complexes as a further precaution against decomposition.

EXPERIMENTAL PROCEDURE

A Bridgman opposed-anvil high-pressure apparatus was used to subject the powder samples to pressures up to 80 kbar. The samples consisted of wafers of 0.25-in. diameter and a thickness after compaction (to about 4 kbar in a pellet press) of about 0.007 in. Pressures on the sample were calculated from the hydraulic fluid pressure assuming uniform distribution of the pressure across the anvil faces. The validity of the latter assumption is fairly good for anvils of the diameter here employed and is discussed by Dachille and Roy.[12] The samples were first subjected to the maximum pressure of the experiment to ensure compaction. The pressure was then released and all electrical measurements were made as the pressure was again increasing. Successive pressure cycles after the initial high-pressure compaction gave essentially identical results. Resistances of the samples were measured through the anvils on a Keithley Model 610A electrometer. The apparent resistivities ρ' of the samples were calculated by using the equation $\rho'=RA/d$, where R is the measured resistance, A the cross-sectional area, and d the final thickness of the sample measured following the experiment.[13] Because of the large resistance changes with increasing pressure, the change in sample thickness hardly needed to be considered.

The sample and anvils were heated by means of a a split, Variac controlled furnace with a thermocouple placed as close to the sample as possible.

Seebeck voltage measurements were made in the press by heating one of the anvils and measuring the potential difference across the anvils with a Model 610B Keithley electrometer. Temperature gradients were of the order of 5° at 30°C as measured by thermocouples fastened to the outside edge of both sample faces. Potential differences due to the anvils, themselves, were negligible compared to potential readings with the sample present. Seebeck coefficients of standard samples [p-type germanium and n-type iron oxide (wüstite)] were measured at low pressures to ensure that the present setup gave comparable Seebeck coefficients to other methods.

The compressibility for pyrene· 0.35 Br_2 was obtained by means of an unsupported piston-cylinder press, the details for which can be found elsewhere.[14,15]

Recorded results are the average taken from several experiments with the spread of resistances in various runs being up to an order of magnitude at the lowest pressures and somewhat less at higher pressures. Activation energies were reproducible to within 0.03 eV, and the Seebeck coefficient variation is shown by vertical lines in Fig. 5.

RESULTS

Plots of apparent resistivity vs pressure for the charge-transfer complexes and polyaromatics are shown in Figs. 1 and 2. The resistances of the latter compounds

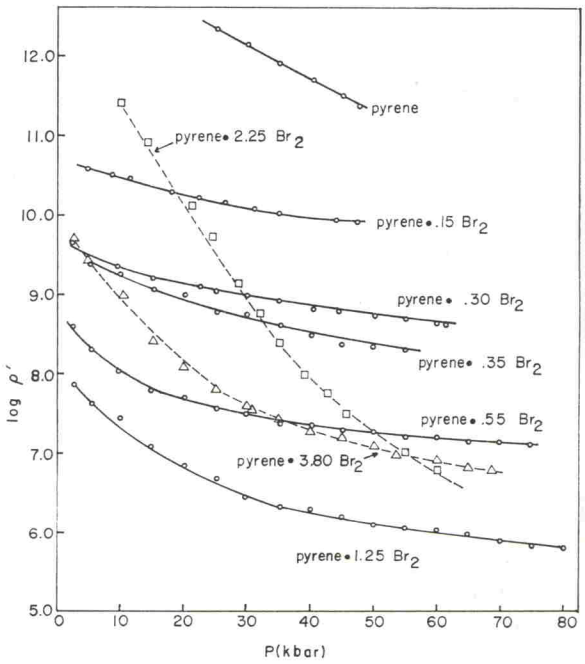


FIG. 1. Apparent resistivity ρ' vs pressure; room temperature.

were not within the range of the measuring instrument for lower pressures. Likewise, the resistance of liquid bromine was far greater than that of the complexes. Log(ρ' vs $1/T$) plots gave straight lines from 20° to 100°C, from which activation energies were calculated on the basis of the equation $\sigma'=\sigma_0' \exp(-E_{act}/kT)$, where σ' is the apparent conductivity. Therefore, the apparent resistivity is given by

$$\rho'=\rho_0' \exp(E_{act}/kT). \quad (1)$$

E_{act}, ρ', and ρ_0' at 12 kbar are shown as a function of bromine content in the complexes in Fig. 3. At this

[11] H. Inokuchi and H. Akamatu, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, p. 141.

[12] F. Dachille and R. Roy, Phys. Chem. High Pressure, Papers 77 (1963).

[13] The resistance values reported here are corrected for the geometry of the pellet in order that they may be approximately compared with resistivity values obtained by other workers. They differ from resistivities because of pressure gradients across the anvils, the samples' changing thickness with pressure, and because powder samples were used.

[14] F. R. Boyd and J. L. England, J. Geophys. Res. **65**, 741 (1960).

[15] G. C. Kennedy and R. C. Newton, *Solids Under Pressure*, edited by W. Paul and D. M. Warschauer (McGraw-Hill Book Company, Inc., New York, 1962), p. 163.

pressure contact resistances should be eliminated, but the low-pressure trend with composition does not appear to have changed. For the pyrene· 1.25 Br_2 sample the activation energy was measured as a function of pressure and is shown in Fig. 4, along with ρ_0'. Activation energy as a function of compression is shown in Fig. 5 for the same complex.

Seebeck coefficients, S, were obtained at low pressures (up to 1.5 kbar) for perylene·Br_2, pyrene· 0.5 Br_2, pyrene· 1.25 Br_2, and pyrene· 1.8 Br_2, and in all cases S was negative (n type). The Seebeck values were of the order 10^{-3} V deg^{-1} at 30°C and all decreased as pressure increased. A systematic pressure effect on

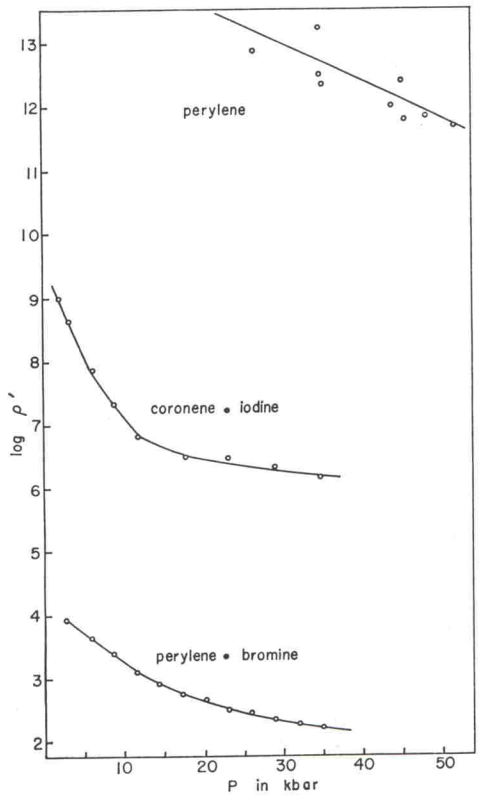


FIG. 2. Apparent resistivity vs pressure; room temperature.

S was measured for pyrene· 1.8 Br_2, and the results are shown in Fig. 6, along with simultaneous resistance measurements. The dashed line shows the initial compression following pellet formation, while the solid line corresponds to compression during the second and third cycles. Measurements were made only for increasing pressure and the time between successive runs was approximately 1 h.

DISCUSSION

The measured resistances (or at least the resistance changes) are indicative of the bulk sample barrier rather than sample–anvil contact barriers, as shown further by the following observations: (1) substituting

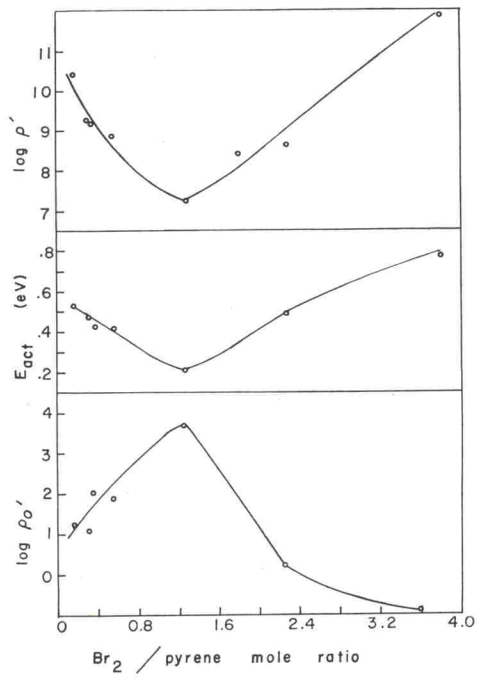


FIG. 3. Apparent resistivity, activation energy, and ρ_0' [see Eq. (1)] as a function of Br_2 content in the pyrene–bromine complex. $P=12$ kbar; room temperature.

Cu, Au, and Pt contacts between the sample and the carboloy anvils gave identical results; (2) the resistances obtained by applying different potentials across the samples was independent of potential up to 10^4 V cm^{-1} (the highest studied); (3) resistance values for the complexes under a N_2 atmosphere were identical to those in air (the polyaromatic compounds had to be pressed under N_2 in order to prevent explosion of the sample); (4) resistivity measurements on single crystals of 2-perylene· $3I_2$ by Kommandeur and Hall[4] were equal to those on pressed pellets. Conductivities have further been shown for similar complexes to be electronic and not ionic, by electrolysis experiments.[1,5]

A decrease in the resistivities of pyrene, perylene, and coronene with increasing pressure is typical of

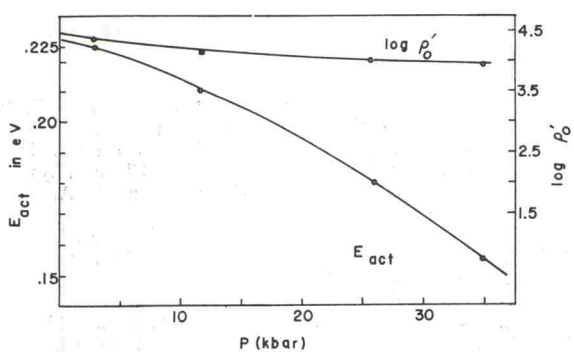


FIG. 4. Activation energy and ρ_0' as a function of pressure for pyrene·1.25 Br_2.

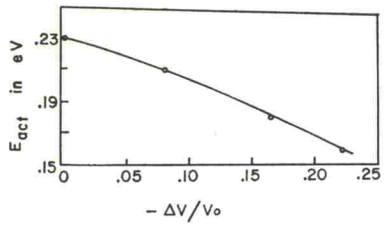


FIG. 5. Activation energy vs compression for pyrene· 1.25 Br_2.

large conjugated systems.[16–20] The increase in conductivity as the π orbitals of adjacent molecules are caused to increasingly overlap one another has been associated either with production of carriers[20] or with carrier mobility.[17] With increasing pressure, the resistance of iodine decreases due to an energy gap decrease and hence to carrier production.[21,22] Bromine presumably behaves similarly, although data for it is not available. Although the resistance of the parent compounds decreases with increasing pressure the range of values for the intermolecular complexes is completely different at a given pressure, and hence the behavior of the complexes is not explained by bulk properties of either parent compound.

Structural studies and density measurements of several intermolecular charge complexes indicate that alternate stacking of donor and acceptor molecules occurs.[5,23–26] Under uniaxial pressure, preferred orientation of the crystallites in the powder occurs[4,5] with the basal plane parallel to the anvil faces. Thus, the resistance measurements through the anvils should be similar to those on single crystal material, going through the chain of alternating aromatic and halogen molecules.

The good semiconductor behavior of charge-transfer complexes at atmospheric pressure is explained by a very much larger number of charge carriers than are present in aromatic compounds as evidenced by high spin populations (about 1 spin per 10 molecules)[4,26] and low mobilities.[3,4,26,27] The low mobility is understandable considering the weak molecular interaction in the complexes; the latter leads to limited electron exchange and hence to charge localization. The exponential temperature dependences of spin concentration of perylene and pyrene iodine complexes is in excellent agreement with the activation energy for electronic conduction, and each unpaired spin is thus identified with a charge carrier.[4,6] Consequently the major contribution to the experimental activation energy at atmospheric pressure is carrier production.

Both positive (hole) and negative (electron) carriers contribute to the over-all conductivity σ. Thus

$$\sigma = n_+ \mid e \mid \mu_+ + n_- \mid e \mid \mu_-, \tag{2}$$

where n_+ and n_- are the concentrations of mobile positive and negative carriers, respectively, and μ_+, and μ_- are their mobilities; e is the electronic charge. The Seebeck coefficient, S, is likewise composed of contributions from both types of carriers and is given by

$$S = [(\Delta E_+ n_+ \mu_+) - (\Delta E_- n_- \mu_-)/\mid e \mid T(n_+\mu_+ + n_-\mu_-)], \tag{3}$$

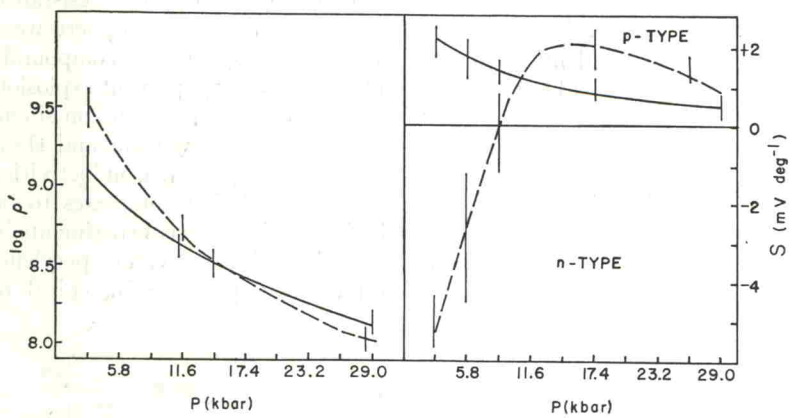


FIG. 6. Apparent resistivity vs pressure (left) and Seebeck coefficient vs pressure (right) for pyrene· 1.8 Br_2. Dashed line represents first pressure cycle. Full line represents second and third pressure cycles.

[16] R. E. Harris, R. J. Vaisngs, H. Stromberg, and G. Jura, Progr. Very High Pressure Res., Proc. Intern. Conf., Bolton Landing, Lake George, New York, 1960, 165 (1961).
[17] R. S. Bradley, J. D. Grace, and D. C. Munro, Phys. Chem. High Pressure, Papers 143 (1962).
[18] G. A. Samara and H. G. Drickamer, J. Chem. Phys. **37,** 471, 474 (1962).
[19] M. A. Cook, R. F. Keyes, A. G. Funk, and F. A. Olson, Naval Ordnance Test Station Final Technical Report, December 1963, 31 Contract N123(60530)-25906A.
[20] R. B. Aust, W. H. Bentley, and H. G. Drickamer, J. Chem. Phys. **41,** 1856 (1964).
[21] A. S. Balchan and H. G. Drickamer, J. Chem. Phys. **34,** 1948 (1961).
[22] B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. **37,** 446 (1962).
[23] O. Hassel, J. Mol. Phys. **1,** 241 (1958).
[24] O. Hassel and H. Stromme, Acta Chem. Scand. **13,** 1781 (1959).
[25] J. C. A. Boeyens and F. H. Herbstein, J. Phys. Chem. **69,** 2153 (1965).
[26] H. Akamatu and H. Inokuchi, *Symposium on Electrical Conductivity in Organic Solids,* edited by H. Kallmann and M. Silver (Interscience Publishers, Inc., New York 1961), p. 69.
[27] N. B. Hannay, *Semiconductors* (Academic Press Inc., New York 1963), p. 424.

ΔE_+ and ΔE_- are the total energies (potential and kinetic) transported by + and − carriers from the hot to the cold metal–semiconductor junction across the temperature difference T. The potential-energy transfer is the energy difference between the Fermi level and the edge of the band in which carriers move. Representing these energies for the valence and conduction bands by E_v and E_c, respectively, and calling E_f the Fermi energy, then,

$$\Delta E_+ = (E_f - E_v) + AkT,$$
$$\Delta E_- = (E_c - E_f) + AkT. \quad (4)$$

The term AkT represents the kinetic energy transferred by the carriers, and A is a constant, the value of which depends upon the factors which control the mobility.

The Seebeck coefficient for pyrene· 1.8 Br_2 changes sign upon initial compaction of the sample (dashed line, Fig. 6) and thereafter the effect of increasing pressure is to decrease the positive S. In accordance with conductance measurements, [Fig. 6 and Eq. (2)] the initial change of sign of S can be explained by an increase in n_+ or μ_+ in Eq. (3). The decrease of the positive Seebeck coefficient with increasing pressure is explained by an increase in μ_- or an increase in n_-. If the carriers do not originate from impurities, an increase in n_- results from a decrease in ΔE_- since

$$n_- = N_- \exp -(E_c - E_f)/kT, \quad (5)$$

(where N_- is the effective density of states). However, n_- increases faster than $(E_c - E_f)$ decreases. We may physically explain the Seebeck results as follows. The hole conduction, in the unoriented, noncompacted powder is possibly inhibited by trapping by the crystallite boundaries. As pressure is applied, the crystallites are oriented and compacted causing removal of these traps such that holes can conduct better than electrons. Electrons must be trapped by some other process (perhaps by halogen molecules). At higher pressures (and at lower pressures for compacted pellets) intrinsic conductivity increases as P increases leading to a decrease in the Seebeck coefficient. Upon release of high pressure, the crystallites in the powder remain compacted and oriented (in agreement with x-ray findings on other charge-transfer complexes).[3]

That pressure affects only E_{act} and not ρ_0' (see Fig. 4) is further evidence that pressure increases the number of carriers, when the agreement between spin concentration and $\log\sigma$ with T variation[6] is considered. From Fig. 3 it is seen that E_{act} and hence carrier production is also the term affected most by a change in halogen concentration.

The energetics of the above phenomena can be understood by extending Mulliken's treatment of molecular compounds[28] to the solid state. The energy of the ground state of two nonbonding molecules, such as pyrene and bromine, is decreased by resonance with an ionic state in which an electron is transferred from the donor to the acceptor molecule. The potential-energy curves may be depicted schematically as in Fig. 7, in which Curve I represents the state in which only dispersion and repulsion forces operate. The charge-transfer state (Curve II) is essentially ionic and pressure tends to increase the stability of the more dense ionic state. Curve III, which extends into a new dimension, shows the conductance state of a charge as the system rearranges to move the electron away from its point of origin. There is also an energy barrier associated with charge migration which must be added to the energy of carrier formation. The electrostatic energy $(E_C - E_B)$ for migration of charge away from neighbor molecules is small and insensitive to conditions compared to the energy $(E_B - E_A)$ of transferring charge thermally between molecules. Changes in the thermal energy of ionization $(E_B - E_A)$ are much smaller than, but naturally parallel, changes in the charge-transfer spectra corresponding to the energy $(E_{B'} - E_A)$. The charge-transfer spectra involves large energies because of the Franck–Condon principle according to which the atoms haven't time to reorganize and to thus ionize with the small expenditure of energy $(E_B - E_A)$. The position of Curve II changes with respect to Curve I as the composition of the molecular complex changes. As the Br_2 to pyrene ratio increases from 0 to 1.25 the ionization energy $(E_C - E_A)$ decreases, passes through a minimum and then increases. This last composition shifts to larger ratios than 1.25 with pressure.

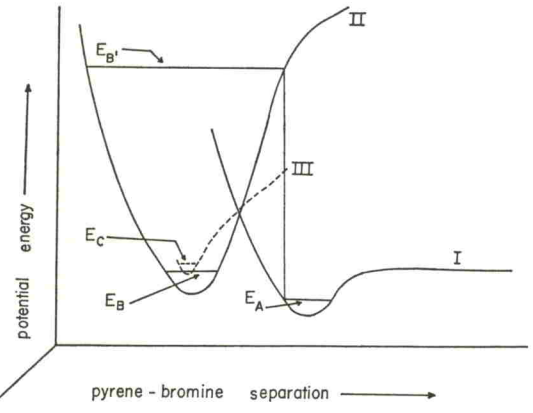


FIG. 7. Potential-energy diagrams indicating typical states of intermolecular charge complexes which are important in electron transport. Curve I: no bond state; Curve II: ionic, charge-transfer state; Curve III: conductance state (charge on different molecule from parent; curve in different dimension from I and II).

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[28] R. S. Mulliken, J. Am. Chem. Soc. **74**, 811 (1952).