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THEORY OF THE PRE-EXPONENTIAL FACTOR IN ORGANIC SEMICONDUCTORS

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ABSTRACT

Tunnelling through intermolecular barriers from activated energy levels of molecules is postulated to be the conduction mechanism in some organic semiconductors. The compensation rule follows immediately from this model. The relationship between the characteristic temperature on one hand, and the barrier shape, height, width and the effective mass of the electrons on the other, is established. It is shown that the triangular barrier assumption gives a reasonable agreement with experiment, in contrast with the square barrier. Estimates of the barrier height, width and effective mass are given. The experimentally sound correlation between σ_0 and the characteristic temperature acquires a physical basis.

I. INTRODUCTION.

The electrical conductivity of semiconductors is given by the formula

$$\sigma(T) = \sigma_0 \exp (-E/2kT) \quad (1)$$

σ_0 is called the pre-exponential factor. This will prove to be a misnomer, since it contains exponential functions. It was first noted by Many, Harnik and Gerlich⁽¹⁾ that the pre-exponential factor σ_0 and E for a large number of organic semiconductors show a correlation. Guttman and Lyons⁽²⁾ found that a linear relationship of the form

$$\log \sigma_0 \approx \alpha E + \beta \quad (2)$$

holds, where for an entire class of substances α and β are constants. This kind of formula was also found by Cardew and Eley⁽³⁾. Some data and discussion of this problem was provided by Eley⁽⁴⁾. Recently Rosenberg, Bhowmik, Harder and Postow⁽⁵⁾ showed evidence that this formula is valid for a single organic substance. E is varied by hydration and complex formation, but σ_0 and T_0 remain invariant. We wish to discuss this formula in the form

$$\sigma(T) = \sigma'_0 \exp (E/2kT_0) \exp (-E/2kT) \quad (3)$$

often called the compensation law, so that

$$\sigma_0 = \sigma'_0 \exp (E/2kT_0) \quad (4)$$

T_0 is called the 'characteristic temperature'.

Eley⁽⁴⁾ considered various mechanisms for the explanation of the pre-exponential factor without drawing firm conclusions. One of these mechanisms is tunnelling through intermolecular potential barriers. We shall show here that this model can account for the data presented in references (4) and (5), and is also reasonable on theoretical grounds.

The agreement between this theory and experiment is not good enough to constitute definite proof of the theory. This is due to the scarcity and the quality of the experimental data and also to oversimplifications in the model. Nevertheless we believe the theory is valuable in correlating the presently available data.

It furnishes a framework and provides incentive for further experimental and theoretical work.

II. Tunnelling Model.

—The organic molecular solids in question consist of molecules with potential barriers surrounding them. Electrons have to pass over or through these barriers for a finite electrical conductivity to arise. The first possibility requires high activation energies. The latter requires a long time. Both possibilities lead to low values of conductivity. The evidence shows, as we shall see below, that often a compromise arises by the electrons tunnelling from activated levels of energy E , as measured from the ground state. This makes the effective wall height E_w smaller than the total height E_T , without requiring $E \approx E_T$. It is improbable that electrons will acquire so much energy (E_T) at reasonable temperatures (Fig. 1).

Experimental evidence requires of our model that while E should vary with hydration and the formation of complexes, E_T should remain a constant. A variation of E can be accounted for by the increase of the dielectric constant by hydration^(6,7). This is the low frequency dielectric constant. The state of an electron in a molecule remains unchanged over times of the order of $10^{-12} - 10^{-13}$ sec which allows the ions to relax. The ions have no time to relax during the time t_w spent by the electrons in the barriers which is given by

$$t_w \approx \hbar/E_w \quad (5)$$

If $E_w = 1$ eV, we find $t_w < 10^{-15}$ sec. The relevant quantity is the high frequency dielectric constant which we shall approximate by unity. Thus we only have to assume that hydration and complex formation do not affect the value of E_T , leaving it a molecular quantity.

We may consider then $\sigma(T)$ to consist of the following factors: 1) the temperature dependent exponential factor, 2) the exponential part of the barrier

transmissivity and 3) a factor σ_x consisting of the non-exponential part of the barrier transmissivity and of the propagation characteristics of the electrons within the molecules. The last factor shall not receive detailed consideration in this paper. We shall employ the barrier transmissivity calculations of Mott and Sneddon⁽⁸⁾. Formula a) shall refer to the square barrier and b) to the triangular barrier. The conductivity then will appear in the alternative forms:

$$\sigma(T) = \sigma_x \exp \left(- \frac{2a}{h} [2m^* E_w]^{1/2} \right) \exp (-E/2kT) \quad (6a)$$

and

$$\sigma(T) = \sigma_x \exp \left(- \frac{4a}{3h} [2m^*]^{1/2} \frac{E_w^{3/2}}{E_T} \right) \exp (-E/2kT) \quad (6b)$$

where m^* is the effective mass of the electron in the activated level involved in the tunnelling. The other parameters are defined in Fig. 1. If one chooses the square barrier, E_T must logically be chosen equal to the ionization potential of the molecule. In reality the tunnelling electron will feel a potential which is the sum of the approximate coulomb potential attracting the electron to a positive ion and the potential of electron affinity of the originally neutral molecule. These potentials vary smoothly and are better approximated by the triangular than by the square barrier. The triangular barrier also provides an extra parameter because now the height of the barrier E_T can be less than the ionization potential. For the logical consistency of the model, $E < E_T$ must be required otherwise there would be no tunnelling, but electrons would pass over the barrier. It is possible that $E > E_T$ would also lead to a compensation law. This point requires further investigation.

On the basis of the foregoing discussion we substitute

$$E_w = E_T - E \quad (7)$$

into eqs. (6) and expand the fractional powers of E_w in a power series stopping at the term linear in E . This yields:

$$\sigma(T) = \sigma_x \exp \left(- \frac{2a}{h} [2m^* E_T]^{1/2} \right) \exp \left(\frac{a}{h} \left[\frac{2m^*}{E_T} \right]^{1/2} E \right) \exp [-E/2kT] \quad (8a)$$

and

$$\sigma(T) = \sigma_x \exp \left(-\frac{4a}{3\hbar} [2m^* E_T]^{1/2} \right) \exp \left(\frac{2a}{\hbar} \frac{[2m^*]^{1/2} E}{E_T} \right) \exp [-E/2kT] \quad (8b)$$

If $E < E_T$ but close to it a better approximation may be necessary. This also requires further investigation.

Comparison with Eq. (3) shows that

$$\frac{1}{2kT_0} = \frac{a}{\hbar} \left(\frac{2m^*}{E_T} \right)^{1/2} \quad (9a)$$

and

$$\frac{1}{2kT_0} = \frac{2a}{\hbar} \left(\frac{2m^*}{E_T} \right)^{1/2} \quad (9b)$$

respectively. These formulae account for the fact that T_0 is always positive⁽⁵⁾.

Comparing Eqs. (3) and (8a) and (8b) we find that

$$\sigma'_0 = \sigma_x \exp \left(-\frac{2a}{\hbar} [2m^* E_T]^{1/2} \right) \quad (10a)$$

and

$$\sigma'_0 = \sigma_x \exp \left(-\frac{4a}{3\hbar} [2m^* E_T]^{1/2} \right) \quad (10b)$$

which by the substitution of Eqs. (9a and 9b) turn into

$$\sigma'_0 = \sigma_x \exp \left(-\frac{2E_T}{2kT_0} \right) \quad (11a)$$

and

$$\sigma'_0 = \sigma_x \exp \left(-\frac{1}{3} \frac{2E_T}{2kT_0} \right) \quad (11b)$$

respectively.

— If we assume now that σ_x and E_T are constant while σ'_0 and $1/2kT_0$ can change from one substance to another then the slope of $\log \sigma'_0$ plotted against $1/2kT_0$ should yield E_T by Eqs. (11a and 11b). The data on Fig. 2 do not allow us to draw a unique straight line. This does not come as a surprise since σ_x and E_T can vary from one material to another. A measure of the situation can be obtained by trying different straight lines. Lines 1 and 2, which utilize data in part from materials where the compensation rule plays no role yield $E_T \approx 1$ eV for the square

and $E_T \sim 3$ eV for the triangular barrier. Line 3, which uses data only from materials where the compensation rule is important, leads to $E_T \sim 2$ eV for the square and $E_T \sim 6$ eV for the triangular barrier. Only the last number is acceptable within the tunnelling model because only this value assures that the activation energies^(4,5) are well below the top of the barrier. Also E_T is in the range of, although possibly somewhat smaller than, the ionization potentials which is a physically reasonable result. For most of the materials considered here the $E < E_T$ requirement is comfortably satisfied. Therefore from here on we shall only consider the triangular barrier. We may now utilize eq. (9b) to obtain the estimate

$$m^* a^2 \approx 10^{-40} \text{ g cm}^2 \quad (12)$$

If we take $m^* = m_e$ we find $a = 3 \times 10^{-7}$ cm which is too large for intermolecular separation. If we take $m^* = 100 m_e$ we obtain $a \approx 3 \times 10^{-8}$ cm which is quite reasonable. Therefore we draw the conclusion that the effective mass of the electron in the activated level is of the order of one hundred electron masses, which puts quite a strain on band theory. An electron with such a large effective mass has an average mean free path of a few tens of angstroms or less. Since the molecular potential well is at least of this size the quantum mechanical potential well model breaks down. The propagation of the electron within a molecule has to be described by a diffusion equation approach. This does not invalidate our present considerations which only apply to the exponential factors and do not examine σ_x .

This work differs from Eley's in two respects. First, we use Fig. 2 to determine the height of the intermolecular barrier to be about 6 eV rather than postulate it to be 20 eV. Also we choose m^* so that it should fit the experimental data rather than arbitrarily require $m^* = m_e$.

IV. Future Outlook.

While we feel that the qualitative agreement of our model with experiment

is satisfactory, the quantitative agreement leaves much to be desired. For this purpose it will be necessary to take more experimental data which are reliable.

In order to find a theoretical estimate of σ_x one will have to consider the diffusion of electrons within the organic molecules, with the tunnelling taking place when the electron is within one mean free path from the wall. In view of the high effective mass of the electrons in the activated band one cannot maintain the customary picture of coherent electron wavefunctions spanning the entire potential well. The coherence of such wavefunctions is destroyed by electron-phonon scattering which requires a particulate description of the electron within the molecular potential well, while maintaining the quantum mechanical description of the tunnelling process itself. Since the external d.c. field causing the current can be easily screened out by slight changes in the charge distribution within each molecule, but not in between the molecules, the conducting electrons diffuse through the individual molecules and change their potential energy upon tunnelling. Thus, in contrast to inorganic materials, we expect the effective d.c. potential to be discontinuous, being constant inside the molecules and changing at the walls. The construction of this more complete model is being contemplated.

A recent publication of M. E. Green (9), using the charge carrier injection by tunnelling through a surface barrier, shows an approximation method which leads to equation (2) above. However, it does not attack the problem of the relation of σ_0 and $1/2kT_0$ as does our present theory.

Since the mass of the proton is only about 20 times the effective mass of the electron and E_T for proton tunnelling should be of the same order as for electrons one can expect that proton tunnelling should play a role in phenomena like electrical conduction. It should be noticed that E_T and the mass only occur under the square-root in Eqs. (9) and therefore $1/2kT_0$ for protons and electrons should not be very different.

REFERENCES

- 1) A. Many, E. Harnik and D. Gerlich, J. Chem. Phys. 23, 1733 (1955).
2. F. Guttman and L. E. Lyons, "Organic Semiconductors", (Wiley, New York, 1967) pp. 428-435.
3. H. H. Cardew and D. D. Eley, Discussions Faraday Soc. 27, 115 (1959).
4. D. D. Eley, J. Polymer Sci. Pt. C. 17, 73 (1967).
5. B. Rosenberg, B. B. Bhowmik, H. C. Harder and E. Postow, J. Chem. Phys. 49, 4108 (1968).
6. B. Rosenberg, J. Chem. Phys. 36, 816 (1962).
7. B. Rosenberg and E. Postow, Ann. N. Y. Acad. Sci. 158, 161 (1969).
8. N. F. Mott and I. N. Sneddon, "Wave Mechanics and Its Applications" Dover New York (1963).
9. M. E. Green, J. Chem. Phys. 51, 3279 (1969).

FIGURE CAPTIONS

Fig. 1. The square barrier a) and the triangular barrier b)

Fig. 2. Plot of the $\log_{10} \sigma'_0$ vs. $1/2kT_0$ for a number of substances.

○ Data points from Ref. 5.

◻ Data points from Ref. 4. [The lower point is computed from Table I and the higher from the line referring to proteins and amino acids in Figure 1].

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b