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ELECTRICAL AND SPECTROPHOTOMETRIC PROPERTIES OF CHARGE-TRANSFER COMPLEXES OF SOME ANTHRACENE DERIVATIVES

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ABSTRACT

The solid charge-transfer (CT) complexes of some anthracene derivatives with nitroaromatic acceptors were prepared. The ionization potential IP, electron affinity EA and energy of the CT transition for the donors, acceptors and CT complexes respectively were determined from the spectrophotometric measurements. In addition, the electrical properties of the CT complexes were investigated. The positive temperature coefficient of electrical conductivity ($d\sigma/dT$) found for all samples provides evidence of their semiconducting properties. A correlation between the spectrophotometric and conductivity parameters was established. The mechanism of the conduction process in these complexes was also studied.

INTRODUCTION

The majority of organic solids studied for their electrical properties are charge-transfer (CT) complexes. There are a large number of publications dealing with the physical properties of these systems [1,2]. A knowledge of the chemical and electrical features is of particular importance for their commercial use in highly efficient solid state batteries [3] and in energy storage [4].

The resistivities of CT complexes formed between polynuclear hydrocarbons and trinitrobenzene, tetracyanoethylene or iodine have been studied [5–8]. The resistivities of these complexes vary from relatively high values (approximately 10^{17} Ω cm) to lower values (2–3 Ω cm). It has been suggested that the basic arrangement of the donor and acceptor moieties consists of layers of alternate donors and acceptors. This suggests that the semiconductivity in these complexes is anisotropic [9]. Recently, numerous investigations have been carried out to determine the unusual metal-like conductivity in organic CT complexes formed between tetrathiafulvalene and tetracyanoquinodimethane (TTF– TCNQ) and their analogues [10].

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The study reported here concerns the electrical and optical properties of solid CT complexes formed between some anthracene derivatives (donors) and nitroaromatic compounds (acceptors).

EXPERIMENTAL

The chemicals employed were of AnalaR grade (BDH). They were used without further purification. The 1 : 1 (donor : acceptor) charge-transfer complexes were prepared using a typical procedure which involves the mixing of equimolar amounts of solutions of the donor and acceptor. Elemental analysis, melting point determination and IR spectroscopy were carried out [11] to confirm the formation and stoichiometry of the complexes. The electronic absorption spectra were recorded on a Unicam SP 8000 UV–visible spectrophotometer using the Nujol mull technique.

The electrical resistivities were measured using a Super Megohmmeter (model RM 170) electrometer. The measurements were carried out on discs (diameter, 13 mm; thickness, 2–3 mm) of the powdered CT complexes at a pressure of about 700 kg cm^{-2}. Good contact was achieved by painting liquid silver on the two opposite surfaces of each disc. The temperature was measured in air using a Cu/CuNi Comark thermometer placed close to the sample. The induced currents at different applied voltages were measured at room temperature to establish the $I-V$ characteristics of some of the CT complexes under investigation.

The anthracene derivatives used as donors were: (a) 9-bromoanthracene, (b) 9-cyanoanthracene, (c) 9-acetylanthracene, (d) 9-carboxylicanthracene, (e) 9-aldehydeanthracene and (f) 9-methylanthracene. The acceptors used were: (1) picric acid, (2) 3,5-dinitrosalicylic acid, (3) 3,5-dinitrobenzoic acid, (4) 1,3-dinitrobenzene and (5) 2,4-dinitrophenol.

RESULTS AND DISCUSSION

The electronic absorption spectra of the donors, the acceptors and the CT complexes were measured. The spectra of the CT complexes exhibit an absorption CT band (λ_{CT}) which does not exist in the spectra of the donors or acceptors within the range 440–510 nm. The energies E_{CT} of these CT transitions were calculated and are listed in Table 1. In addition, the ionization potentials IP of the donors and the electron affinities EA of the acceptors 2, 3 and 5 were determined using Briegleb procedures [12]. These are shown in Table 2. It can be shown that the ionization potentials of the donors are dependent on the inductive effect of the substituents. The electron affinities increase in the order $2 > 5 > 3$ which can be explained on

TABLE 1

The charge-transfer band (λ_{CT} (nm)) and the corresponding charge-transfer energy (E_{CT} (eV)), the activation energies (ΔE_1 and ΔE_2 (eV)), the transition temperature (T_s (° C)) and the energy gap (E_g (eV)) of the CT complexes under investigation

Complex [a]	λ_{CT} (nm)	E_{CT} (eV)	Heating cycle				Cooling cycle			
			ΔE_1 (eV)	ΔE_2 (eV)	T_s (° C)	E_g (eV)	ΔE_1 (eV)	ΔE_2 (eV)	T_s (° C)	E_g (eV)
a_1	510	2.440	0.863			1.706				
b_1	485	2.560					0.990			1.980
e_1			1.440	4.076	62	2.880	1.443	3.689	58	
d_1	500	2.490					0.594			
c_1	480	2.590	2.853			5.706	2.828			
f_1	510	2.440	1.575			3.150				
f_2	490	2.538	1.881			3.762	1.889			
f_3	480	2.590	2.121			4.242				
f_4	440	2.830	2.835			5.669				
f_5	485	2.564	2.039			4.078				

[a] The letter represents the donor; the number represents the acceptor.

TABLE 2

The donors and acceptors under investigation and their deduced ionization potentials IP and electron affinities EA respectively

Donor		IP (eV)	Acceptor		EA (eV)
9-Bromoanthracene	(a)	7.350	Picric acid	(1)	0.7 [4]
9-Cyanoanthracene	(b)	7.370	3,5-Dinitrosalicylic acid	(2)	0.543
9-Acetylanthracene	(c)	7.397	3,5-Dinitrobenzoic acid	(3)	0.490
9-Carboxylicanthracene	(d)	7.397	1,3-Dinitrobenzene	(4)	0.3 [9]
9-Aldehydeanthracene	(e)	7.293	2,4-Dinitrophenol	(5)	0.517
9-Methylanthracene	(f)	7.373			

the basis of the increasing electron withdrawing and steric effects of the substituents.

The variation in the electrical resistivities of the CT complexes with temperature was measured on heating. Measurements were also obtained on cooling after raising the temperature to just below the melting point. In addition, measurements were carried out during heating and cooling cycles for CT complexes of donors (c) and (e) with picric acid and of donor (f) with 3,5-dinitrosalicylic acid. The electrical conductivity σ can be deduced using the equation

$$\sigma = \frac{1}{R} \times \frac{d}{A} \tag{1}$$

where R is the electrical resistance (ohm) and d and A are the thickness and cross-sectional area of the powder disc respectively. Figures 1 and 2 represent the variation in the electrical conductivity (log σ) as a function of reciprocal temperature $1000/T$ (K^{-1}). It can be shown that there is a positive coefficient of the electrical conductivity ($d\sigma/dT$) for all samples under investigation. Therefore, all complexes possess semiconducting properties. The dependence of the electrical conductivity on temperature satisfies the well-known equation

$$\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{kT}\right) \tag{2}$$

where σ is the electrical conductivity at a given absolute temperature, σ_0 is the initial conductivity (the pre-exponential factor), ΔE is the activation energy and k is the Boltzmann constant.

It is worth noting that all the CT complexes possess one region of conduction, except the CT complex of donor (e) with picric acid. Consequently, this complex has two activation energies (ΔE_1 and ΔE_2) with temperature transitions within the range 58–62° C. The values of activation energy were deduced and are listed in Table 2. It can be seen that the activation energies in the temperature–conductivity profiles obtained for some CT complexes during heating and cooling cycles are in close agree-

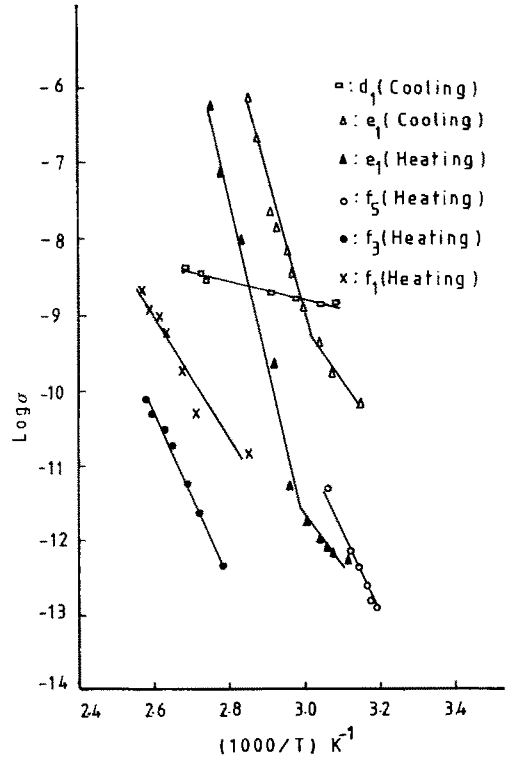

Fig. 1. The variation in electrical conductivity as a function of reciprocal absolute temperature for d_1, e_1, f_1, f_3 and f_5 CT complexes on heating and cooling.

ment. Therefore there is no chemical interaction between the donors and acceptors of the CT complexes.

It has been established that the activation energy of conduction decreases with increasing conductivity of the compound. Therefore, the activation energy should increase with a decrease in the electron affinity [13]. As can be seen in Fig. 3, the activation energies of the CT complexes of 9-methylanthracene are inversely proportional to the electron affinities of the acceptors 1–5. In addition, it is obvious from Table 2 that the energy gaps of the relevant complexes are higher than the charge-transfer excitation energies. Consequently, it is reasonable to propose that the conduction process involves the excitation of a π electron from the highest filled π orbital to the lowest empty molecular orbital. This is in agreement with the previous studies carried out by Eley et al. [14]. In some instances the energy gaps for conduction are unexpectedly low in comparison with the charge-transfer transition energy, e.g. the CT complexes of picric acid with donors (a), (b) and (d). For these complexes the energy levels lying below those of the charge-transfer excited state must contribute to the electrical conductance [8].

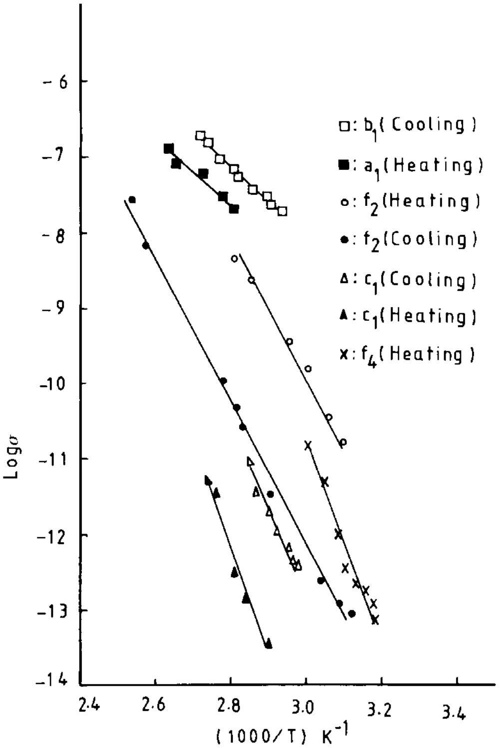

Fig. 2. The variation in electrical conductivity as a function of reciprocal absolute temperature for a_1, b_1, c_1, f_2 and f_4 CT complexes on heating and cooling.

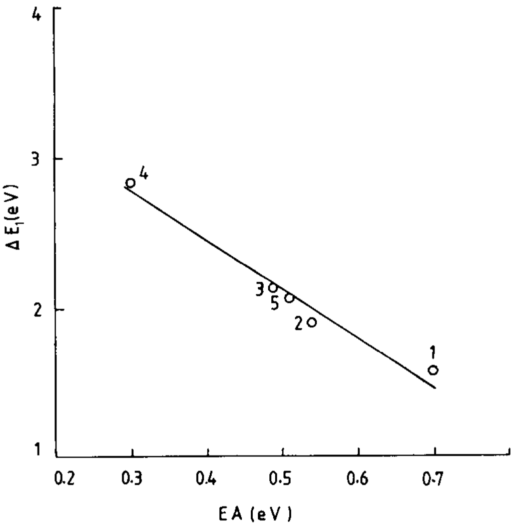

Fig. 3. The variation in the activation energy of conduction (ΔE_1) as a function of the electron affinity of the acceptors.

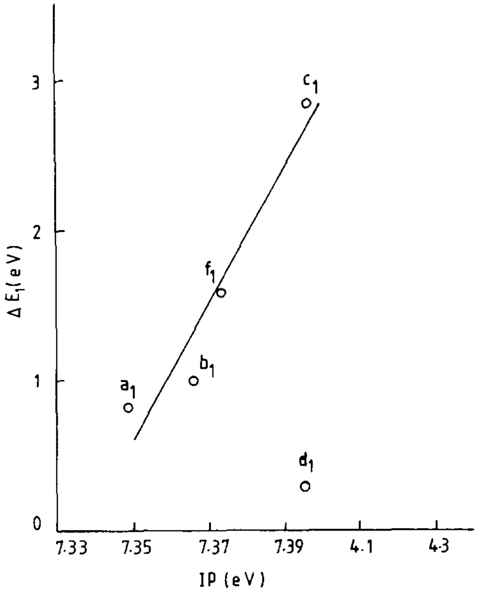

Fig. 4. The variation in the activation energy of conduction (ΔE_1) as a function of the ionization potential of the donors.

The electrical conductivities and activation energies of complexes of different donors with picric acid are dependent on the ionization potential of the donors. Figure 4 shows a plot of ΔE_1 vs. IP of the donors for the relevant CT complexes; the plot is linear. This may be explained on the basis of the increased electron density and polarization of the donor mole-

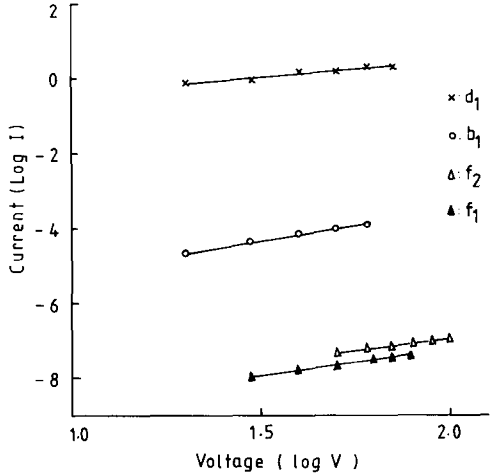

Fig. 5. The current–voltage ($I-V$) characteristics of some CT complexes.

cule as a function of the electron donating or attracting character of the substituent. Thus this may enhance the ionization mechanism and electron flow.

When potential differences *V* were applied for some CT complexes, a current *I* was measured. *I*–*V* characteristics of these complexes are shown in Fig. 5. It can be shown that CT complexes of donors (b), (d) and (f) with picric acid and of donor (f) with 3,5-dinitrosalicylic acid have ohmic character (obey Ohm's law).

GENERAL CONCLUSIONS

The ionization potentials of the donors and the electron affinities of some of the acceptors were determined. In addition, the investigation of the electrical conductivities of the CT complexes revealed the semiconducting properties of all the complexes. The spectrophotometric determination of E_{CT}, IP and EA and the activation energy ΔE deduced from the conductivity measurements are in agreement. The mechanism of the conduction in these CT complexes is dependent on the energy of the CT transition.

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