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ELECTRICAL PROPERTIES OF CHARGE TRANSFER COMPLEXES OF 2-AMINOPYRIMIDINE AND 2-AMINOPYRAZINE SCHIFF BASES WITH NITROBENZENE DERIVATIVES

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ABSTRACT

A study of the electrical properties of charge-transfer (CT) complexes of 2-aminopyrimidine and 2-aminopyrazine Schiff bases with nitrobenzene derivatives has been done. The investigation comprises the 1:1 as well as the 1:2 donor:acceptor (D:A) complexes. The behaviour of the electrical conductivity for all CT complexes in the studied range of temperatures indicates a semiconducting character.

The 1:1 CT complexes show higher electrical conductivity values with respect to those of the corresponding Schiff bases due to the increased π-electron delocalization in the CT complexes. The decrease of activation energy in dinitrobenzene CT complexes with respect to the corresponding Schiff base is lower than that observed in trinitrobenzene derivatives. This confirms that the molecular complexes of the former are much weaker than the latter.

The 1:2 complexes are characterized by higher activation energy values (lower electrical conductivity) with respect to the corresponding 1:1 complexes: a behaviour which is due to participation of both rings in CT leading to an increased localization of the π-electrons.

There is a correlation between the dielectric constant for most of the studied CT complexes and their electrical conductivities.

INTRODUCTION

Electrical conduction in organic molecular solids [1] differs in several important ways from that in metals and typical semiconductors, like silicon and germanium. Actually, no really satisfactory theory of organic conduction has yet emerged, but it is clear that the molecular nature of organic solids dictates their electrical properties. There are four principal types of organic conductors, namely, conjugated chains, free radicals, charge-transfer (CT) complexes and organometallic compounds.

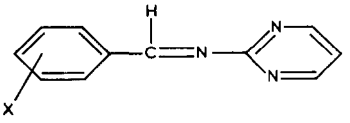
Charge carriers are most readily formed by the activation of non-bonding or π-bonded electrons, which, when being delocalized in a conjugated system, form an internal conduction path of high mobility. In the case of solid CT complexes, two types of conduction are distinguished. A large number of solid CT complexes formed from non-radical electron-donor and electron-acceptor species are diamagnetic and are very poor electrical conductors [2].Complexes of such a type are usually composed of components, one at least of which is a relatively weak interactant. On the other hand, there are solid complexes involving strong donor and strong acceptor species which are paramagnetic. The latter show some indications of ionic character in their ground state. There is no evidence that the mechanism of carrier generation is only intrinsic. Such behaviour may arise in various ways, e.g. (a) through surface generation of charge carriers and injection, (b) by small polaron formation with hopping transport or (c) there may be extrinsic semiconductors.

Abou Sekkina and Issa [3] prepared several 1 : 1 CT complexes by the reaction of trinitrobenzene derivatives (acceptors) with anil and anil derivatives (donors). The temperature dependence of the direct voltage electrical conductivity has been investigated and the values of specific conduction, activation energy for conduction and energy gap have been evaluated to throw light on the band-structure of materials investigated for their possible use in solar cells. The investigators were able to establish a correlation for the electrical and optical properties for the first time.

EXPERIMENTAL

The acceptors used were of pure chemical grade (AR), supplied from BDH (U.K.). The donors and their CT complexes used were prepared from pure chemicals (BDH), analysed, and their characteristics established by chemical analysis, melting points, infrared and ultraviolet absorption spectra measurements.

The solid CT complexes were prepared directly from their corresponding ethanolic solution of acceptors and donors. Experimental details for the preparation of the CT complexes [4–6] were followed as previously mentioned, but with some modifications for sample purification and recrystallization. The donors used have the following structural formulae



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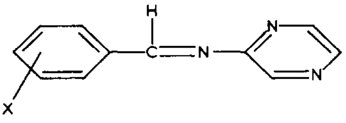


II

where a, X = H; e, X = p–N$(CH_3)_2$; f, X = o–OH. The acceptors encountered in the present study are (1) picric acid, (2) trinitrobenzene and (3) 2, 4-dinitrophenol. The electrical measurements were followed as previously mentioned by the authors [8].

RESULTS AND DISCUSSION

The present discussion is concerned with the CT complexes of 2-aminopyrimidine (I) or 2-aminopyrazine (II) Schiff bases with some nitrobenzene derivatives. The discussion comprises the 1 : 1 as well as the 1 : 2 (D:A) complexes.

The current–voltage characteristic curves give a linear relationship, which indicates that the compounds under investigation have Ohmic character.

The curves obtained for the relationship between electrical conductivity and temperature for the CT complexes are represented graphically in Figs. 1 and 2. It is obvious that the electrical conductivity increases with continuous increase of temperature according to the relation [8]:

$$\sigma = \sigma_0 \, e^{-\Delta E/KT}$$

Since this equation is also obeyed by inorganic semiconductors, it may also be used to describe the electrical properties of organic materials (CT complexes). Such an assumption is justified if it is known that the charge carriers are not ionic.

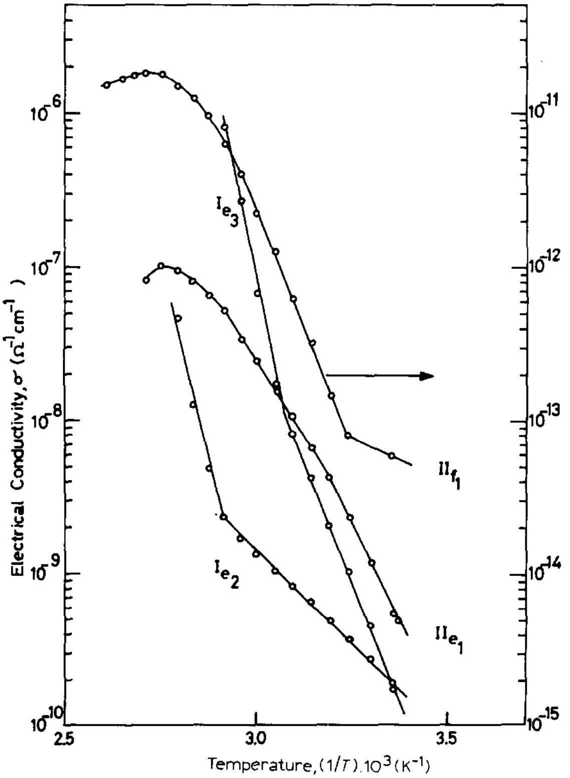


Fig. 1. The electrical conductivity as a function of temperature for some 1 : 1 CT complexes with nitrobenzene derivatives.

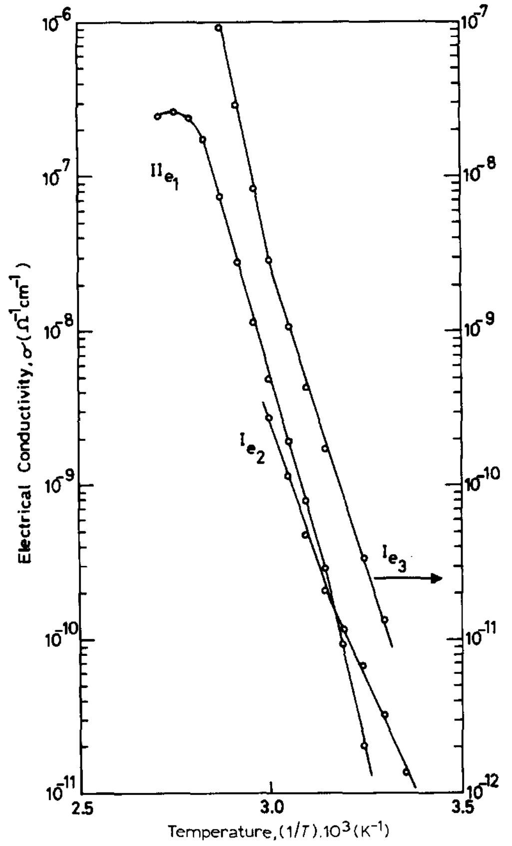


Fig. 2. The electrical conductivity as a function of temperature for some 1 : 2 CT complexes with nitrobenzene derivatives.

Most of the obtained temperature dependent electrical conductivity curves of the complexes are characterized by two activation energy values (Table 1). This means that the mode of conduction is changed during conductivity measurements. It is thus assumed that the first step in the conduction process is essentially due to electronic conduction through the delocalization of the π-electrons. While for the second step, occurring at high temperatures, the conduction is due to the excitation of an electron from the uppermost filled π-molecular orbital to the lowest unfilled π-molecular orbital. Thus, the electron is assumed to tunnel to an equivalent empty level of a neighbouring molecule in the anodic direction, whereas the positive hole moves to a molecule in the cathodic direction.

The electrical conductivity depends largely on the chemical structure of the compounds investigated (Table 1). The results may be summarized as follows:

(a) The electrical conductivity values of the CT complexes (1 : 1) are generally higher than those of the corresponding free Schiff bases (Table 2).

TABLE 1

Electrical conductivities σ (Ω^{-1} cm^{-1}) at room temperature, and the activation energies ΔE (eV) for the CT complexes with some substituted tri- and dinitrobenzene acceptors

Complex		Melting point (°C)	σ at room temperature (Ω^{-1} cm^{-1})	Activation energy (eV)	
				Low temperature range	High temperature range
CT complexes of picric acid					
Ia	(1:1)	229	6.8×10^{-10}	0.62	0.97
	(1:2)	220	1.4×10^{-11}	1.02	0.72
Ie	(1:1)	202	1.6×10^{-9}	0.31	1.35
	(1:2)	163	2.8×10^{-10}	1.48	0.29
IIf	(1:1)	229	5.8×10^{-14}	0.22	1.18
IIe	(1:1)	231	6.8×10^{-10}	1.03	0.78
	(1:2)	130	1.3×10^{-12}	2.28	1.72
CT complexes of trinitrobenzene					
Ie	(1:1)	98	2.0×10^{-10}	0.49	2.01
	(1:2)	81	1.6×10^{-11}	1.09	1.50
IIf	(1:1)	65	6.3×10^{-12}	0.21	0.10
CT complexes of 2, 4-dinitrophenol					
Ie	(1:1)	82	2.1×10^{-10}	0.92	2.50
	(1:2)	104	5.2×10^{-12}	1.56	2.56

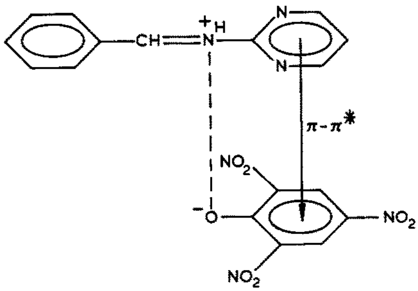
This is probably attributable to the increased π-electron delocalization in the charge transfer complexes.

(b) Almost all picric acid complexes (1 : 1) exhibit a remarkable increase in electrical conductivity with respect to the corresponding Schiff bases. This can be explained by the fact that picric acid forms complexes through electron transfer from the donor to the acceptor, in addition to proton transfer from the acceptor to the donor.

TABLE 2

Electrical conductivities σ (Ω^{-1} cm^{-1}) at room temperature and the activation energies ΔE (eV) for the investigated Schiff bases (donors)

Donor	Melting point (°C)	σ at room temperature (Ω^{-1} cm^{-1})	Activation energy (eV)	
			low temperature range	high temperature range
Ia	188	1.4×10^{-13}	0.26	0.46
Ie	63	7.4×10^{-11}	1.38	2.12
IIf	108	1.5×10^{-12}	0.89	1.25
IIe	60	6.6×10^{-10}	1.29	2.11



This configuration indicates, presumably, that the lone pair electrons of the nitrogen atom are no longer capable of contributing to the conduction process.

A remarkable decrease of conductivity is observed in such complexes with increase of temperature (above 90 °C) (Figs. 1 and 2). This may be explained by a change of the structure of the CT complex which may occur through the depolarization of the azomethine N^+–H group leading to the formation of a weaker complex through π–π * electronic interaction only.

(c) For complexes of trinitrobenzene (1 : 1), an increase of the electrical conductivity, with respect to the corresponding free Schiff bases, was observed. This is most probably attributable to the increased number and mobility of charge carriers which are most readily formed by the activation of non-bonding or π-bonded electrons [3]: since they are delocalized in a highly conjugated system, they form an internal conduction pathway of high mobility.

(d) The activation energy of 2, 4-dinitrophenol (1 : 1) complexes is higher than most picric acid and trinitrobenzene complexes (Table 1). This is in accordance with the fact that the molecular complexes of 2, 4-dinitrophenol are weaker than the picric acid and trinitrobenzene complexes, a behaviour which depends on the electron affinities of the acceptors. The electron affinity E_A of 2, 4-dinitrophenol is 0.5 eV [7], while that of both picric acid and trinitrobenzene is 0.7 eV [3]. Thus, the complex formed with the former acceptor is weaker than the others. The 1 : 2 (D:A) complexes are characterized by higher activation energies than the corresponding 1 : 1 complexes. A behaviour which is due to the participation of both heterocyclic amino and benzal rings in CT, leading to an increased localization of the π-electrons. Consequently, a decrease of electrical conductivity is observed.

The dielectric properties of the CT complexes are also studied, it is found that the dielectric constant ϵ increases with temperature.

Figure 3a, b shows the dielectric constant, ϵ, of CT complexes with picric acid IIe_1 and IIf_1 (1 : 1) and IIe_1(1 : 2). We notice that IIf_1 (1 : 1) has the lowest ϵ. IIe_1 (1 : 2) has a lower dielectric constant, than IIe_1 (1 : 1) in the temperature range considered (from room temperature to ≈ 80 °C); it then

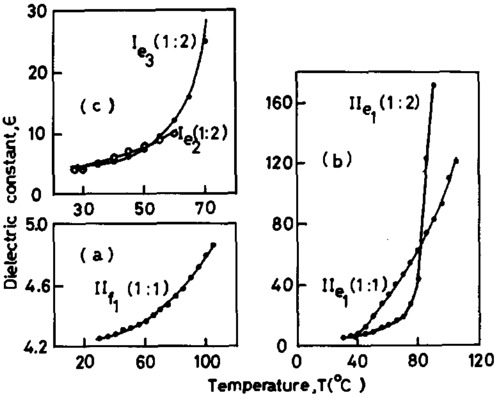


Fig. 3. The dielectric constant as a function of temperature for some 1:1 and 1:2 CT complexes: (a, b) with picric acid; (c) with trinitrobenzene Ie_2 and 2, 4-dinitriphenol Ie_3.

increases. Figure 3c shows the behaviour of the dielectric constant for CT complex Ie_2 (1 : 2) of trinitrobenzene, and Ie_3 (1 : 2) of the 2, 4-dinitrophenol CT complex: they have almost the same ϵ up to 60°C.

The previous results are in very good agreement with the electrical conductivity measurements of the same CT complexes.

The dielectric constant, as shown in Fig. 3a–c, is strongly dependent on the chemical structure of CT complexes.

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