

Electrical and thermal behaviour of some Schiff bases and their charge transfer complexes with acidic acceptors

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Abstract

The electrical conductivities of some Schiff bases and their charge transfer complexes (CTCs) with 2,4-dinitrophenol and picric acid as acidic acceptors indicate that they behave as semiconductors within the investigated range of temperature. However, they are insulators at 300 K. DTA and IR spectra show the importance of the solvent of crystallization molecules in lowering the activation energy of the acceptors and the CTCs. The linear free energy relationship (LFER) indicates that the conduction process depends on the electronic structure.

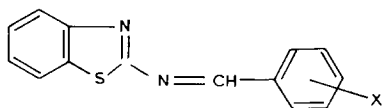
INTRODUCTION

Electron-donor and electron-acceptor-forming CTCs can stack independently (segregated system, S) or alternately (mixed system, M). The S systems display electrical conductivities ranging from those typical of semiconductors to those of metals; some of them become superconductors at low temperatures [1]. The M systems, however, display a particular neutral–ionic phase transition [2]. Since the discovery of metallic conductivity in CTCs, considerable interest has been focussed on their potential application as semiconductors [2,3]. There are two essential requirements that must be met: that the charge transfer (CT) molecules crystallize in separate segregated stacks, and that the charge transfer from donor to acceptor be incomplete [4].

The X-ray crystal structure and conductivity of CTCs of *m*- and *p*-dinitrobenzene with tetrathiafulvalene have been studied by Bryce et al. [4,5]. These CTCs are neutral 1 : 1 complexes which behave as insulators at room temperature. Also, the CTCs of some di- and trinitrobenzene derivatives with different donors have been investigated [6–8]. However, no study has been made of the electrical conductivity of CTCs derived from Schiff bases as donors with di- and trinitrobenzene derivatives as acceptors. The present investigation reports the study of the electrical conductivity and thermal behaviour of some Schiff bases derived from 2-aminobenzothiazole and of their CTCs with 2,4-dinitrophenol and picric acid.

EXPERIMENTAL

All the chemicals used were of the purest grade available from Aldrich Chemical Company, Inc. (USA). The Schiff bases (I–VIII) were prepared according to the recommended procedure [9] and recrystallized from ethanol. Their identity was established by m.p. determination, IR spectra and elemental analysis. The structural formula of the Schiff bases is



where X = H (I), *p*-N(CH₃)₂ (II), *p*-OH (III), *o*-OH (IV), *p*-Cl (V), *m*-Cl (VI), *p*-Br (VII) and *p*-NO₂ (VIII).

The CTCs were synthesized by mixing a saturated solution of the Schiff base (0.01 mol dm⁻³ in ethanol) with an equivalent solution of 2,4-dinitrophenol (1) (DNP) or picric acid (2) at 40°C. The solids separated were then filtered off and recrystallized from ethanol; the insoluble solids were reboiled with ethanol to ensure removal of unreacted products. The CTCs were dried in a vacuum and preserved in closed tubes over CaCl₂. Their purity and identity were then checked by TLC, m.p. measurements and elemental analysis. The data revealed the formation of 1:1 CTCs of various colours.

The d.c. electrical conductivity measurements of the Schiff bases, acceptors and CTCs were carried out using a Super Megohmmeter Model RM 170 (AVO Ltd., Dover, England). The sample used in the measurements was pressed into a cylindrical pellet, 0.6 cm in diameter and 0.12 cm thick, at a pressure of about 500–600 kg cm⁻². All measurements were checked at least twice in each case, and reproducible data were obtained. The ohmic nature of the contacts was achieved by the linear dependence of the *I*–*V* characteristic curves within the temperature range used and under a range of applied voltage *V* = 10–220 V for all the investigated compounds, with the exception of compounds I, IV, I₁, IV₁, VIII₁, I₂ and III₂. The conduction of the latter compounds exhibits an ohmic nature at 300 K, in the applied voltage range of 5–80 V with *n* = 1.03–1.12, and space charge limited current (SCLC) in the range 80–240 V with *n* = 1.72–1.93. At 355 K, the conduction proceeds with an ohmic nature alone.

RESULTS AND DISCUSSION

The d.c. electrical conductivities (log σ) as a function of the reciprocal of the absolute temperature (1000/*T* K⁻¹) of the Schiff bases (I–VIII) in the solid phase are characterized by one activation energy (ΔE) value, while for DNP and picric acid two activation energy values are obtained,

TABLE 1

The electrical conductivity (σ), activation energy (ΔE) and energy gap (E_g) of the Schiff bases and acceptors 1 (DNP) and 2 (picric acid)

Schiff base	ΔE (eV)	E_g (eV)	$\sigma(300\text{ K})$ ($\text{Ohm}^{-1}\text{ cm}^{-1}$)	Schiff base	ΔE (eV)	E_g (eV)	$\sigma(300\text{ K})$ ($\text{Ohm}^{-1}\text{ cm}^{-1}$)
I	3.60	7.20	3.22×10^{-12}	V	2.80	5.60	3.62×10^{-12}
II	3.20	6.40	2.30×10^{-13}	VI	2.20	4.40	1.38×10^{-11}
III	2.80	5.60	4.38×10^{-12}	VII	2.60	5.20	2.32×10^{-13}
IV	2.63	5.26	1.60×10^{-11}	VIII	0.92	1.84	4.83×10^{-11}
1	0.26	0.52	6.30×10^{-12}	2	0.17	0.34	2.50×10^{-12}
	1.19	2.38			1.19	2.38	

see Table 1. The straight lines and discontinuity of the temperature–conductivity curves can be investigated by IR spectra and DTA measurements. The IR spectra of the dry, solid Schiff bases as KBr discs do not exhibit any bands due to the solvent molecules, in spite of the appearance of a broad band at around 3350 cm^{-1} in the spectra of **III** and **IV** due to the stretching vibrations of the hydroxy group. Also, the DTA curves show no peaks in the temperature range $30\text{--}160^\circ\text{C}$ indicating the thermal stability of these Schiff bases within that temperature range. However, the IR spectra of DNP and picric acid exhibit a weak broad band at around 3500 cm^{-1} due to stretching vibrations of the hydroxy group of moisture, in spite of the fact that they had been dried under vacuum for several days. This is further supported by the DTA endothermic peaks at 115 and 130°C corresponding to the release of the water molecules. It is observed that the discontinuity of the curves occurs at 87°C and $70\text{--}80^\circ\text{C}$ for DNP and picric acid respectively. The differing temperature values of the desolvation process could be ascribed to the lower rate of heating in the conductivity experiments compared with the DTA. The low activation energy values of the solvated acceptor molecules DNP and picric acid are due to the solute–solvent interactions which may lead to a decrease in the scattering behaviour of the charge carriers caused by the lattice vibrations and, hence, to a decrease in the activation energy. However, the desolvated molecules of DNP and picric acid have the same activation energy value, 1.19 eV , indicating that they have the same conduction mechanism.

In all cases there are positive temperature coefficients of electrical conductivity, i.e. a semiconducting character for the Schiff bases (**I–VIII**) and the acceptors 1 (DNP) and 2 (picric acid). The activation energy values can be interpreted by a band model containing a partially occupied set of trap states near the centre of the energy gap between the valence and conduction bands.

The LFERs (linear free energy relationship) between the activation energy values and the Hammett σ constant, Fig. 2, indicate that the

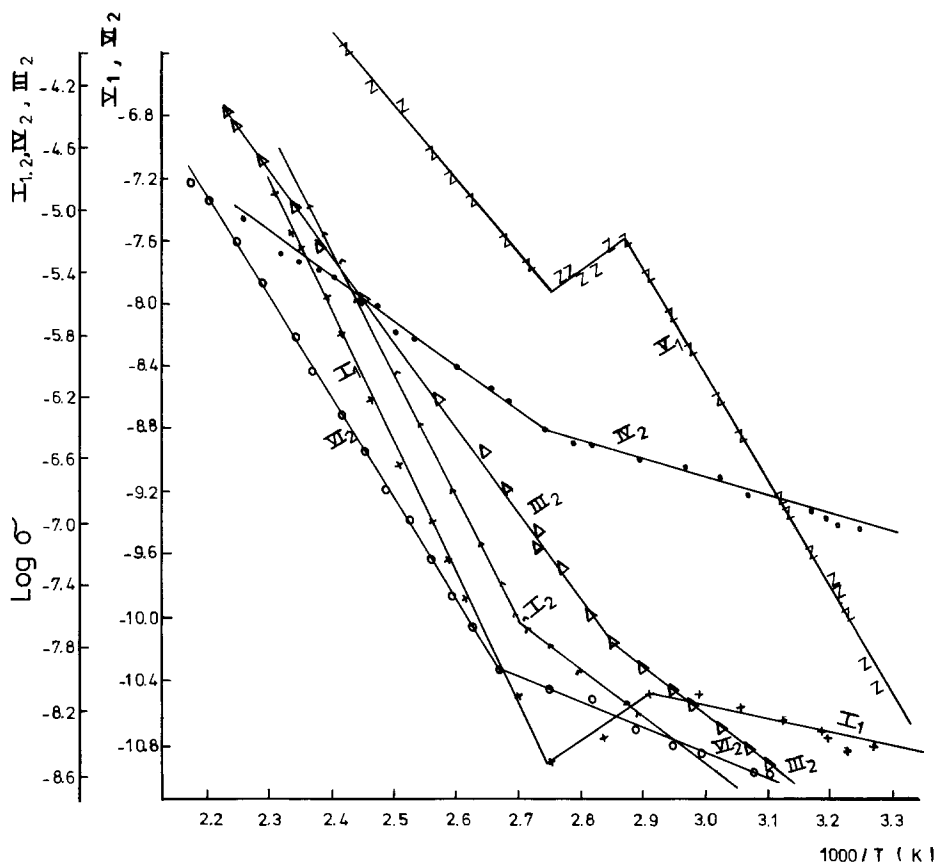


Fig. 1. $\text{Log } \sigma$ versus $1000/T$ for some CTCs.

conduction process depends on the electronic structure. The electron-donating and -accepting substituents cause a decrease in activation energy values. However, the magnitude of the decrease in activation energy values caused by electron-accepting substituents is higher than that caused by electron-donating groups. The activation energy values of the hydroxy derivatives show negative deviation from linearity due to hydrogen bonding which causes partial alignment of molecules leading to an increase in dipole moment within the molecule.

The temperature dependence conductivity curves of CTCs (I–VIII)₁ and (I–VIII)₂, Fig. 1, show two activation energy values within the temperature range 30–180°C, with the exception of CTCs II_{1,2} and VII_{1,2} which are characterized by one activation energy, see Tables 2 and 3, because at low temperature values the points are scattered. All the CTCs reveal a conventional semiconducting behaviour because the conductivity increases with increasing temperature within the investigated range. The discontinuity or scattering phenomena in the temperature conductivity curves of the CTCs

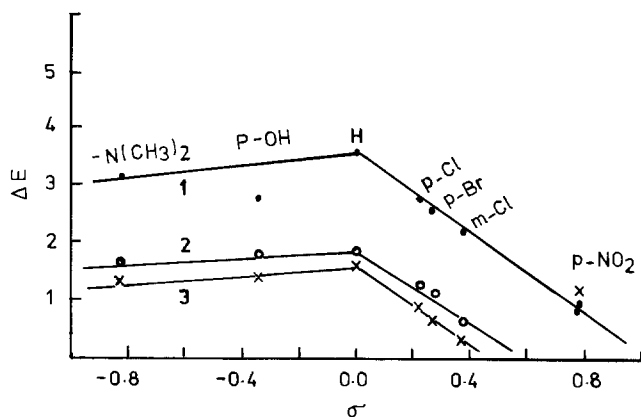


Fig. 2. The LFER between ΔE and σ for Schiff bases (1), CTCs derived from DNP (2) and CTCs derived from picric acid (3).

TABLE 2

Colour, m.p., electrical conductivity (σ), activation energy (ΔE), energy gap (E_g) and transition temperature (T) of CTCs derived from DNP

CTC	Colour	m.p. (°C)	ΔE_1 (eV)	E_{g1} (eV)	ΔE_2 (eV)	E_{g2} (eV)	σ (300 K) ($\text{Ohm}^{-1} \text{cm}^{-1}$)	T (°C)
I ₁	Pale yellow	160	0.22	0.44	1.84	3.68	3.16×10^{-9}	69–89
II ₁	Yellow	128	–	–	1.66	3.32	2.30×10^{-10}	87
III ₁	Yellow	153	0.45	0.90	1.80	3.60	1.58×10^{-11}	88
IV ₁	Faint orange	125	0.14	0.28	1.49	2.98	1.51×10^{-10}	70–80
V ₁	Yellow	140	0.99	1.98	1.30	1.60	2.99×10^{-11}	65–89
VI ₁	Yellow	130	0.35	0.70	0.66	1.32	1.77×10^{-10}	66–94
VII ₁	Yellow	148	–	–	1.20	2.40	4.53×10^{-10}	69–89
VIII ₁	Canary yellow	173	0.86	1.72	0.92	1.84	1.50×10^{-11}	91

TABLE 3

Colour, m.p., electrical conductivity (σ), activation energy (ΔE), energy gap (E_g) and transition temperature (T) of CTCs derived from picric acid

CTC	Colour	m.p. (°C)	ΔE_1 (eV)	E_{g1} (eV)	ΔE_2 (eV)	E_{g2} (eV)	σ (300 K) ($\text{Ohm}^{-1} \text{cm}^{-1}$)	T (°C)
I ₂	Yellow	152	0.61	1.22	1.60	3.20	1.31×10^{-10}	95
II ₂	Yellow	205	–	–	1.36	2.72	5.01×10^{-10}	91
III ₂	Yellow	177	0.92	1.84	1.30	2.60	4.67×10^{-10}	78
IV ₂	Orange	230	0.20	0.40	0.60	1.20	7.94×10^{-8}	90
V ₂	Orange	180	0.71	1.41	0.90	1.80	1.99×10^{-11}	84
VI ₂	Yellow	192	0.32	0.64	1.16	2.32	6.31×10^{-12}	100
VII ₁	Yellow	160	–	–	0.62	1.24	1.77×10^{-10}	86
VIII ₂	Golden yellow	177	1.04	2.08	1.24	2.48	5.62×10^{-12}	104–140

are due to the solvent molecules of crystallization, as seen from the IR spectra and DTA measurements. A broad band at around 3450 cm^{-1} due to the stretching vibrations of the solvent molecules appears in the IR spectra of the CTCs. This band disappears in the spectra of the heated samples. In addition, the DTA curves of the CTCs show an endothermic peak in the temperature range $95\text{--}140^\circ\text{C}$ corresponding to the release of the solvent molecules of crystallization from the CTCs.

The activation energies of the CTCs are lower than the corresponding values of the Schiff bases. Complexation facilitates the mobility of electrons and, hence, increases the conductivity of the complexes. In the case of the CTCs, the energy gap between the valence band, which is the HOMO of the donor moiety in the CTC, and the conduction band, which is the LUMO of the acceptor moiety in the CTC, is narrower than that between the valence and the conduction bands of the donor or the acceptor. However, the CTCs derived from picric acid exhibit lower activation energies than the corresponding CTCs derived from DNP, see Fig. 1 and Tables 2 and 3. This may be attributed to the higher acidic character of picric acid ($pK = 0.38$ [10]) compared with DNP ($pK = 4.09$ [10]), which facilitates the resonance stabilization of proton transfer between the proton of the hydroxy group of the acceptor and the nitrogen atom of the azomethine group [6]. The occurrence of this phenomenon was confirmed by the appearance of a new band in the range $3100\text{--}3075\text{ cm}^{-1}$ corresponding to $\nu(=\overset{+}{\text{N}}\text{--H})$, in addition to the $\nu(\text{OH})$ band of picric acid at 3120 cm^{-1} and of DNP at 3320 cm^{-1} . Furthermore, the electron affinity (EA) of picric acid ($\text{EA} = 1.450\text{ eV}$ [6]) is higher than that of DNP ($\text{EA} = 1.11\text{ eV}$ [6]), which leads to a decrease in the energy gap between the HOMO of the donor and the LUMO of the acceptor.

The LFER between the activation energy of the CTCs and the Hammett σ constant, Fig. 2, shows the same behaviour as observed with the Schiff bases. However, the conductivity values at 300 K do not obey this relationship and have low values in spite of the relatively low activation energy values. This unexpected feature indicates that the conductivity at low temperatures is affected by the presence of solvent of crystallization molecules in these CTCs. In conclusion, these CTCs are insulators at 300 K , as demonstrated by their conductivity values and IR spectra, which consist of sharp peaks typical of insulating complexes [4]. Thus, these CTCs do not have the required properties for high conductivity.

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