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Temperature and structure effects on the electrical conductivity properties of some azo compounds and their copper(II) complexes

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The electrical conductivity of some 5-(*m*-substituted phenylazo) barbituric acid derivatives as well as their copper(II) complexes has been measured in the temperature range 297 to 443 K. The results revealed semiconducting properties for these systems. The conductivity curves in most cases gave two different activation energies. Both the structure of the ligand and the temperature played an effective role in the conduction process. Empirical equations correlating the activation energy to the conductivity are given. The mobility was calculated and a hopping model is proposed to explain the conduction process.

1. Introduction

Azo compounds have widespread applications in many fields of interest, e.g. analytical, dyeing processes and as model examples in biological systems. This paper is a report of a continuation of our study of the physico-chemical properties of azo compounds and their transition metal complexes [1–6] and in relation to our recent investigations [7–9] dealing with the electrical conductivity properties of the organic ligands along with their metal complexes. It was hoped to shed light on the effects of temperature, substituents and structure on the electrical conductivity behaviour of the new azo compounds and their copper(II) complexes, not reported in the literature.

2. Experimental procedure

The metal-free compounds under investigation were barbituric acid BA (I), and its 5-(*m*-substituted phenylazo) barbituric acid derivatives (II). The azo compounds were prepared and characterized as described previously [10].

A series of copper(II) complexes was synthesized and characterized. These were $Cu_2L \cdot 8H_2O$, Cu_2L, $CuL \cdot H_2O$, $Cu_2L \cdot 5H_2O$ and CuL derived from the ligands X = O, –CHO, R = –CHO, $-CO_2H$, $-CH_3$, –OH and $-NO_2$, respectively.

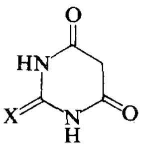
For electrical conductivity measurements samples were prepared in the form of tablets of 0.1 ± 0.01 cm thick at a pressure of 5 ton cm^{-2}. The samples were held between two copper electrodes with a silver paste and then inserted with the holder vertically into a cylindrical electrical furnace. The potential across the heater was varied gradually through a variac transformer to produce a slow rate of increase of temperature in order to obtain accurate temperature measurements. The electrical measuring circuit consisted of Healthkit d.c. regulated power supply (0 to 400 V) and electrometer (Keithley 610 °C) for measuring current with a sensitivity up to 10^{-13} A. The temperature of the samples was measured to within ± 0.1 K using a digital thermometer (Keithley 871 Type KTC NiCr–NiAl). The conductivity of the samples was obtained in the case of cooling using the general equation

$$\sigma = \frac{I}{V_c}\frac{d}{a} \tag{1}$$

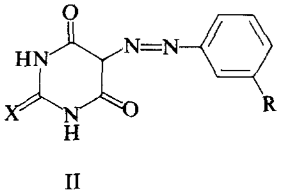
where I is the current (A) and V_c is the potential drop (V) across the sample of cross-sectional area a (cm^2) and thickness d (cm).

3. Results and discussion

Figs 1 and 2 illustrate the variation of the logarithmic electrical conductivity values as a function of reciprocal absolute temperature for the ligands and their



(I)
X = O or S



II
X = O : R = -H, -CHO, -COOH, -Cl, $-NO_2$, $-CH_3$, -OH
X = S : R = -CHO

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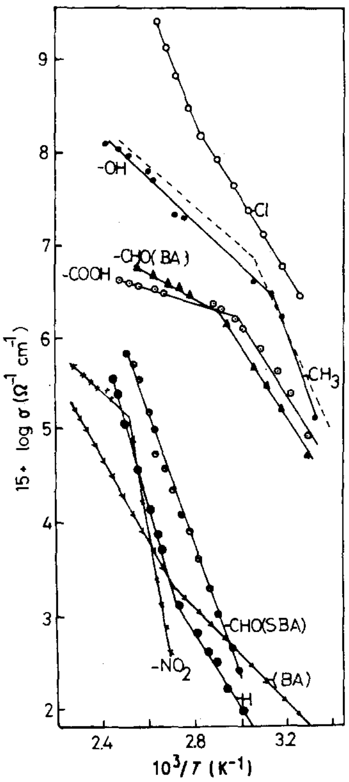

Figure 1 Log σ–$1/T$ relation for the ligands.

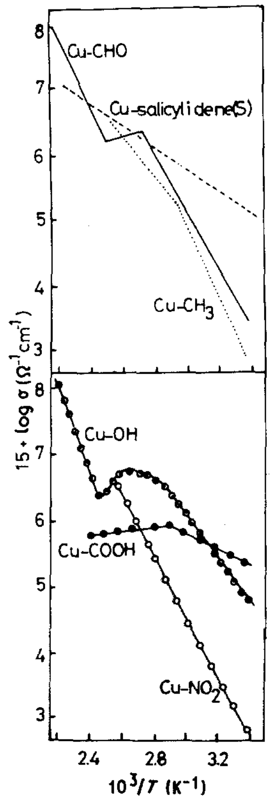

Figure 2 Log σ–$1/T$ relation for copper complexes.

metal complexes, respectively. The measurements fit the following relation

$$\sigma = \sigma_0 \exp(-\Delta E/2KT) \qquad (2)$$

where σ and ΔE were the specific conductivity and the activation energy, respectively. σ_0 and K are constants for the conductivity independent of temperature, and the Boltzmann constant, respectively. Tables I and II give the d.c. electrical conductivity results.

Focusing attention on the $\log \sigma$–$1/T$ relationship for the metal-free ligands, Fig. 1, merits the following comments. Generally the systems under investigation proceed in a similar manner. The conductivity curves showed one segment at a characteristic transition temperature with two different activation energies. However, the data of the *m*-aldehydo phenylazo thiobarbituric acid gave only one straight line, i.e. with only one ΔE value. This implies that the structure of such a compound somehow differs from the others. It has been reported [11] that there is no guarantee that the energy term will be the same for conduction along different crystal directions. Moreover, the magnitude of the energy gap can also be affected by the ambient atmosphere, the presence of impurities, temperature [12] or pressure [13]. It is apparent that ΔE for the systems under investigation is temperature dependent. The phenomenon of the discontinuation in the conductivity curves can be argued to be a molecular rearrangement or crystallographic transition [14]. Careful examination of the conductivity data (ΔE, $\log \sigma_0$ as well as the transition temperature) given in Table I, indicate that the parent barbituric acid (BA) gave two ΔE values (0.50 and 0.97 eV) with a transition temperature at 371 K. However, the 5-phenylazo barbituric acid also gave two ΔE values, but of higher magnitudes (0.78 and 1.61 eV) and a lower transition temperature at 365 K. The data reflect the role played by the phenylazo moiety towards the conducting properties of the parent BA. Furthermore, the nature of the substituents of different electronic requirements in the phenyl ring affects the conductivity data to a great extent, Table I. It could be deduced that $\Delta E_1 < \Delta E_2$ for barbituric acid BA, phenylazo barbituric acid and chloro phenylazo barbituric acid, $\Delta E_1 > \Delta E_2$ for the others (–CHO, –COOH, $-NO_2$,

TABLE I D.c. conductivity data of the metal-free ligands

Compound, substituent (R)	ΔE_1[a] (eV)	ΔE_2[b] (eV)	Log σ_0	Transition temperature (K)
Barbituric acid (BA)	0.50 (0.51)	0.97 (0.97)	1.53	371
–H	0.78 (0.83)	1.61 (1.58)	10.08	365
–CHO (BA)	0.81 (0.80)	0.20 (0.19)	−5.73	342.5
–CHO (SBA)[b]	1.40 (1.49)	–	8.61	–
–COOH	0.80 (0.80)	0.13 (0.13)	−6.70	331
–Cl	1.09 (0.85)	1.39 (1.37)	13.01	353
$-NO_2$	2.67 (2.67)	0.35 (0.40)	−5.28	393
$-CH_3$	1.08 (0.99)	0.44 (0.45)	−1.92	325.5
–OH	1.51 (1.50)	0.47 (0.46)	−1.15	318

[a] Obtained based on least squares method of calculation; those values in parentheses are from the plot.

[b] 5-(*m*-aldehydophenylazo) thiobarbituric acid

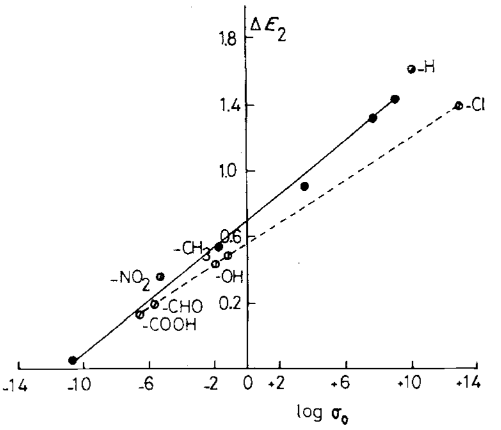

Figure 3 ΔE_2–log σ_0 relation for the (⊘) ligands and (●) the copper complexes.

TABLE II D.c. conductivity data of the copper complexes

Complex	ΔE_1[a] (eV)	ΔE_2[a] (eV)	Log σ_0	Transition temperature (K)
Cu–CHO (BA)	0.92 (0.93)	(1.37)	7.75	365, 398
Cu–COOH	0.31 (0.25)	−0.12 (−0.07)	−10.78	346
Cu–CH_3	1.10 (1.05)	0.55 (0.62)	−1.67	343
Cu–OH	0.68 (0.66)	1.43 (1.32)	8.99	408
Cu–NO_2	0.92 (0.91)	– –	3.43	–

[a] Obtained based on least squares method of calculation; values in parentheses are from the plot.

–CH_3, and –OH). In addition, ΔE_1 for the azo compounds is greater than ΔE_1 for the parent BA. The observed variations in the conductivity characteristics between the 5-(aldehydo phenylazo) barbituric acid ($\Delta E_1 = 0.81$, $\Delta E_2 = 0.02$ eV) with a transition temperature at 342.5 K) and its isostructure 5-(aldehydo phenylazo) thiobarbituric acid, $\Delta E_1 = 1.40$ eV, may be argued to be the electronegativity differences between both oxygen and sulphur atoms. Attempts to correlate ΔE_2 for the organic compounds and their log σ_0 values resulted in a straight line plot, Fig. 3, where the results fit

$$\Delta E_2 = 0.063 \log \sigma_0 + 0.56 \qquad (3)$$

On the other hand, the conductivity curve for the copper 5-(*m*-nitro phenylazo) barbituric acid complex represented in Fig. 2 gave one activation energy value of 0.92 eV. However, the other copper complexes exhibited a discontinuity in their conductivity curves, Fig. 2, with one or two breaks. This can be ascribed to the possible existence of different crystallography or phase transitions [14, 15]. The conductivity data given in Tables I and II clearly indicate that the complexing property affected the values of both energy gaps and the transition temperatures for their corresponding ligands. However, the magnitudes of the conductivities of the ligands and their metal complexes along with the values of the energy gaps favour assignment to a faint semiconducting behaviour rather than metallic conductors, or that promotion of electrons from ground to excited states may be necessary before conduction occurs. In this context, it has been proposed [16] that the first step in the conduction process is the excitation of a π-electron from the uppermost filled π-orbital to the lowest empty πMO. The electron is then assumed to tunnel to the equivalent empty level of the neighbouring molecule in the direction of the anode, whereas the positive hole moves in the opposite direction towards the cathode. If the electron is assumed to arise from the highest MO, it must be placed in a state of different multiplicities in order to become sufficiently long-lived. The first excited singlet and the first triplet state will almost certainly be too far above the ground state to allow thermal population. Hence, it is conceivable that the population of electrons in the lowest unoccupied πMO may be proportional to the absolute energy of the lowest empty orbital in the complexes [17]. However, the polymeric complexes could provide a convenient route for the conduction of charge carriers through chemical bonds rather than tunnelling or charge transfer between molecular species that are not directly bonded. Based on the insolubility of the complexes under investigation in the most common organic solvents, interaction might occur between atoms in a metal–atom chain. In fact, the metal chain complexes have been a topic of considerable interest [18]. On constructing the ΔE_2–log σ_0 relation for the copper complexes, a straight line is obtained, Fig. 3, where the conductivity data fit with the following empirical equation

$$\Delta E_2 = 0.08 \log \sigma_0 + 0.7 \qquad (4)$$

The mobilities, μ, of the ligands and their copper complexes were calculated based on the equation

$$\sigma = eN_0\mu$$

where N_0 is the number of current carriers. $10^{21}\mu$ values for the parent barbituric acid were in the range 10^{-9} to 10^{-12} $cm^2 V^{-1} sec^{-1}$, and between 10^{-5} and 10^{-12} $cm^2 V^{-1} sec^{-1}$ for its substituted phenylazo derivatives. The values of μ for the copper complexes were in the range 10^{-6} to 10^{-11} $cm^2 V^{-1} sec^{-1}$. Because the values of μ were much smaller than 1 $cm^2 V^{-1} sec^{-1}$, the band model is not applicable to describe the mechanism of conductance for the systems under investigation [19]. However, in addition to the fact that in the present system μ increases with temperature, it seems adequate to consider the "hopping model" [20] for the description of the mechanism of conductance.

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