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ELECTRICAL PROPERTIES OF SOME PYRIDINIUM IODIDE DERIVATIVES

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ABSTRACT

The electrical properties of some 1,6-dimethyl-2-[substituted styryl]pyridinium iodide derivatives were studied. The results indicate that the compounds exhibit semiconducting properties. The activation energies of conduction (ΔE) were correlated with the molecular structures. In addition, the current–voltage ($I-V$) characteristics were investigated. The samples have ohmic and/or space-charge-limited conduction (SCLC). These conductions are either temperature dependent or temperature independent.

INTRODUCTION

Organic solids are commonly regarded as electrical insulators since they frequently contain few charged species and exhibit poor overlap between orbitals of neighbouring molecules so that charge cannot pass rapidly from molecule to molecule. However, the most fascinating features of these organic materials is that their physical and electrical properties can be modified by synthetic or solid-state chemical methods [1–3] which have always been followed by a proposal of practical use; for example, electrochemical devices [4], photovoltaic cells [5,6] and their utility in integrated display circuitry or sensors and in electrophotographic copiers [7]. The present investigation was devoted to the study of the electrical and thermal properties of some 1,6-dimethyl-2-[substituted styryl]pyridinium iodide salts. In addition, the current–voltage ($I-V$) characteristics of some samples were studied.

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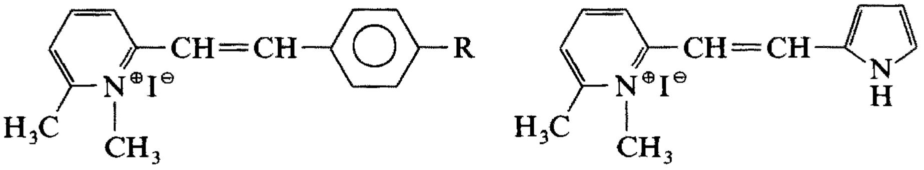
EXPERIMENTAL

The structural formula of 1,6-dimethyl-2-[substituted styryl]pyridinium iodide derivatives is as shown in Scheme 1.



I–VI **VII**

Scheme 1.

where R = H (**I**), OH (**II**), OCH_3 (**III**), $N(CH_3)_2$ (**IV**), Cl (**V**) or NO_2 (**VI**).

The compounds were prepared as described elsewhere [8]. The precipitated compounds were recrystallized several times from a water–ethanol mixture, and then dried under vacuum for several hours. The analyses of the resulting compounds were checked by TLC using neutral aluminium oxide and by melting-point measurements.

The electrical conductivities (σ, Ω^{-1} cm^{-1}) in the temperature range 20–140 ° C and the current (I) for a series of applied voltages (V) within the range $5 < V < 480$ V were measured using a Super Megohmmeter electrometer (model 170) as described previously [9]. The DTA measurements were made using a Du Pont 900 thermal analyser.

The IR measurements were recorded using a Perkin–Elmer spectrophotometer (model 683).

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation in the electrical conductivity (log σ) as a function of reciprocal absolute temperature ($1/T$ K^{-1}) for the 1,6-dimethyl-2-[substituted styryl]pyridinium iodide derivatives (**I**–**VII**). It is evident that the conductivity increases as the temperature is increased, hence all samples possess semiconducting properties.

The dependence of the electrical conductivity on temperature satisfies the conventional equation

$$\sigma = \sigma_0 \exp -\Delta E/KT$$

where σ_0 is constant, ΔE is the activation energy and K is Boltzmann's constant. It can be shown that the plots of log σ versus $1/T$ have either a discontinuity (**II**, **V**, **VI** and **VII**) or some scattering of data points (**I**) in the temperature range 70–120 ° C. The activation energies, ΔE_1 and ΔE_2, deduced from the linear plots below 70 ° C or above 120 ° C, respectively, are

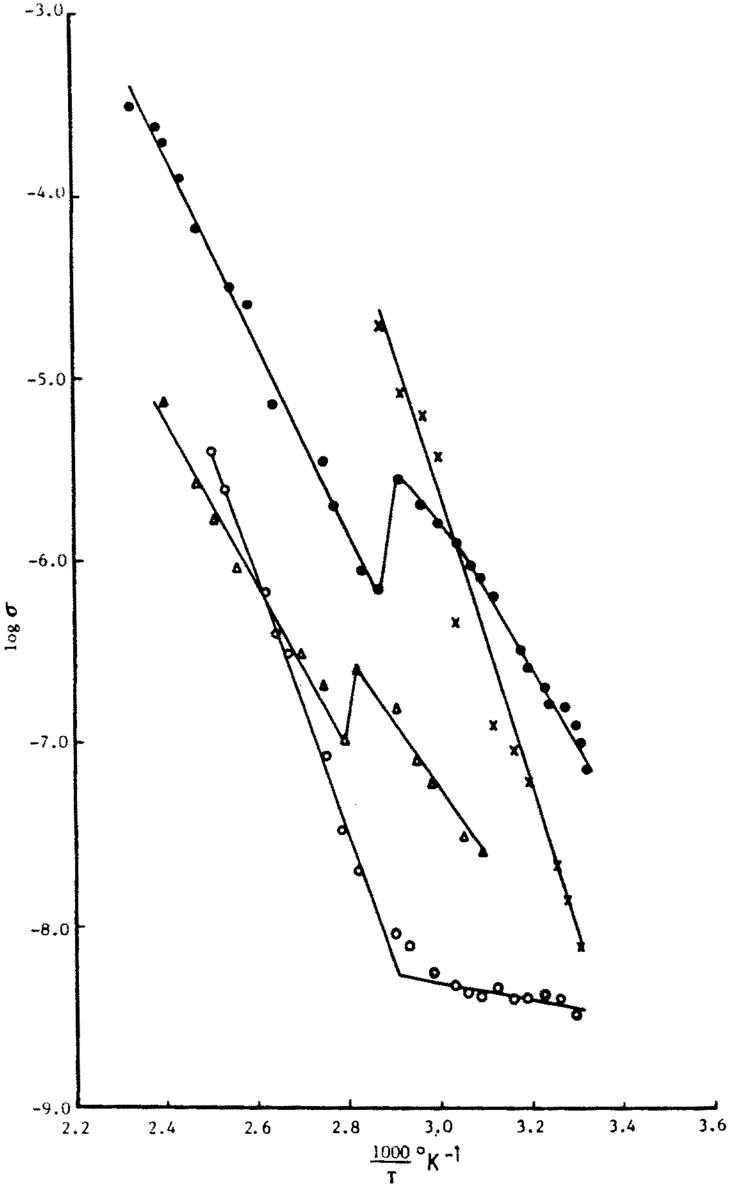


Fig. 1. log σ versus $1000/T$ for compounds: ×, **IV**; ●, **V**; △, **VI**; ○, **VII**.

given in Table 1. The discontinuity or the scattering phenomena of the temperature–conductivity curves were investigated using DTA and IR measurements.

The DTA curves show endothermic peaks at 141, 146, 145, 144 and 100 °C corresponding to the release of the solvent of crystallisation from compounds **I**, **II**, **III**, **IV** and **VI**, respectively. Apart from this peak, the compounds are stable within the temperature range 30–160 °C. At tempera-

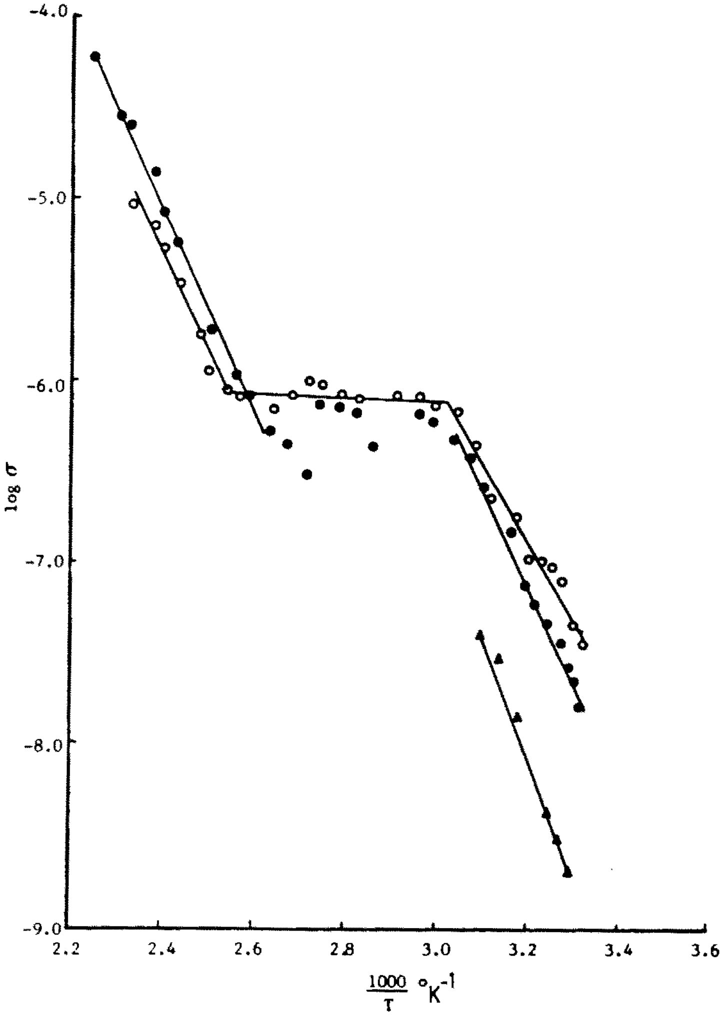


Fig. 2. log σ versus $1000/T$ for compounds: ●, **I**; ○, **II**; ▲, **III**.

TABLE 1

The electrical conductivity at 30 °C (σ_{30}), activation energies (ΔE_1 and ΔE_2) and the transition temperature (T_s) for compounds **I–VII**

Compound	σ_{30} (Ω^{-1} cm^{-1})	ΔE_1 (ev)	ΔE_2 (ev)	T_s (°C)
I	0.25×10^{-9}	1.060	1.067	50–98
II	0.50×10^{-9}	0.848	1.089	56–122
III	2.24×10^{-9}	1.302	–	–
IV	7.94×10^{-9}	1.577	–	–
V	1.25×10^{-7}	0.825	1.056	60–70
VI	5.62×10^{-9}	0.742	0.931	78–88
VII	3.16×10^{-9}	0.099	1.392	70

tures above 160 °C, the curves exhibit an endothermic and an exothermic peak corresponding to the melting and the decomposition of the compound, respectively.

The IR spectra for compounds **I–IV** were measured using KBr discs at room temperature and after heating the sample discs up to 150 °C. At room temperature, a broad band is observed in the IR spectra at around 3430 cm^{-1}. This band disappears in the IR spectra of the heated samples.

Therefore, it is concluded that the discontinuity or scattering of data points in the temperature range 70–120 °C for compounds **I–VI** could be attributed to the release of the solvent molecules of crystallisation. The different temperatures of the desolvation process and the discontinuity or scattering phenomena can be ascribed to the different heating rates used. The rate of temperature increase in resistance measurements was 1 °C min^{-1}, whilst that in the DTA studies was 20 °C min^{-1}.

The activation energy values, ΔE_1, of the solvated samples are slightly lower than those of the desolvated ones. The solute–solvent interactions may lead to a decrease in the scattering behaviour of the charge carriers, owing to the lattice vibrations, and hence to a decrease in the activation energy.

The DTA curve for compound **VII** revealed its thermal stability in the temperature range 30–160 °C. The DTA curve shows an endothermic peak at 169 °C due to melting. The sample then decomposes producing an exothermic peak at 187 °C and an endothermic peak at 206 °C. However, plots of log σ vs. $1/T$ for the compound **VII** show a discontinuity at 71 °C and, therefore, it has two activation energies ΔE_1 and ΔE_2. The discontinuity phenomenon can be ascribed to a molecular rearrangement, crystallographic transition, volume change or changes in conduction mechanism [10]. Therefore, it would be reasonable to suggest that the ΔE values obtained for compound **VII** are due to changes in the conduction mechanism.

Both the activation energy and the conductivity of all the samples studied depend on the substituent (R) on the benzal ring. This was confirmed by plotting ΔE versus the Hammitt substituent constant (σ_R) for compounds **I–VI** (Fig. 3). A linear relationship was obtained with a correlation coefficient of 0.964; however, the hydroxy derivative (**II**) showed a deviation from this correlation. The presence of an electron-withdrawing group in the *para* position on the benzal ring is expected to act as a hand by means of which the electron cloud is drawn from the heterocyclic ring towards the benzal ring. Furthermore, the inductive effect of these substituents should have an impact on the energy band so as to reduce the activation energy. Thus, it might be possible gradually to enhance the transport of charge-carriers within the compound. In contrast, electron-releasing substituents inhibit charge-carrier migration from the hetero ring. The negative deviation observed in the case of the *p*-hydroxy compound (**II**) could be attributed to the possible formation of stacks through hydrogen bonding. This leads to a change in the direction of the dipole moment due to the formation of stacks.

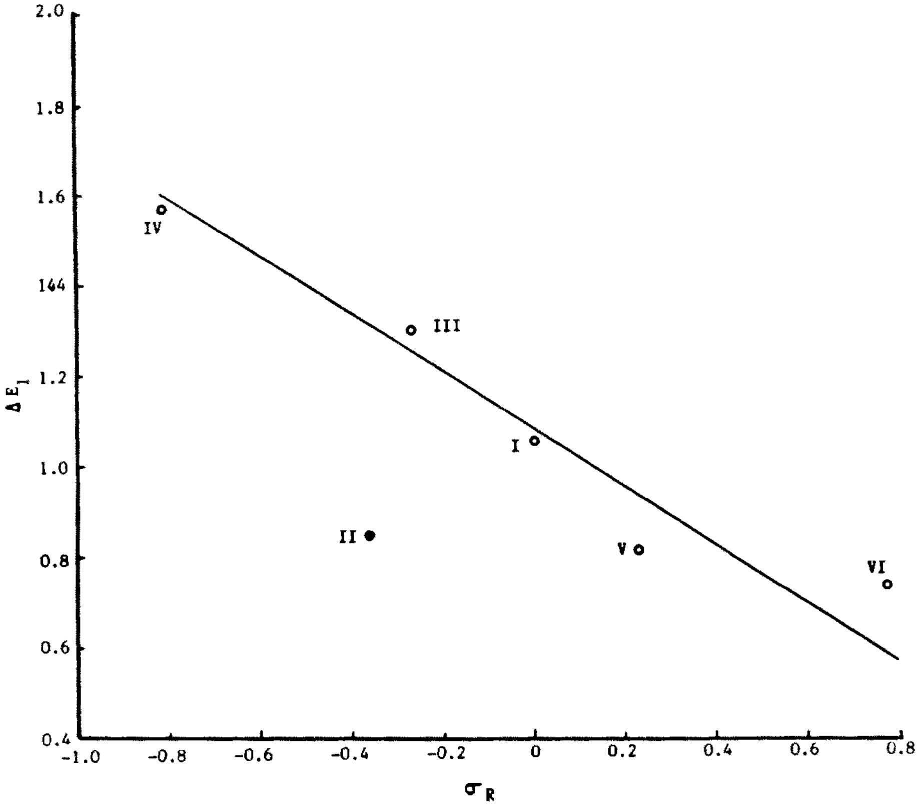


Fig. 3. The relationship between ΔE_1 and σ_R for compounds I–VI.

The plots of log *I* versus log *V* (Fig. 4 and Table 2) for compound **IV** at 35 °C show a $I \propto V^n$ dependence with $n = 1.02$ throughout the applied voltage range studied $10 < V < 80$. This suggests an ohmic conduction [2], whereas at higher voltages ($80 < V < 210$) the points fit the $I \propto V^n$ dependence closely with $n = 1.88$. This suggests space-charge-limited current (SCLC) conduction [2]. The log *I* versus log *V* curves of the *p*-hydroxy (**II**) and *p*-chloro (**V**) derivatives at 35 °C and 30 °C under the applied voltage ranges 10–220 and 10–240 V show $I \propto V^n$ dependence with $n = 1.18$ and 1.29, respectively. This indicates that these samples obey Ohm's law. However, the same plots were studied at 70 °C and 72 °C in the voltage ranges 10–240 and 10–160 V and the deduced values of *n* are 1.15 and 1.06 for the *p*-hydroxy and *p*-chloro derivatives, respectively. Hence, the relevant compounds have ohmic character which is temperature independent over the range of temperatures and voltages applied.

The log *I* versus log *V* plots of the unsubstituted (**I**) and the *p*-methoxy (**III**) derivative (Fig. 4 and Table 2) show anomalous behaviour. The unsubstituted compound proceeds via ohmic, SCLC to nearly ohmic con-

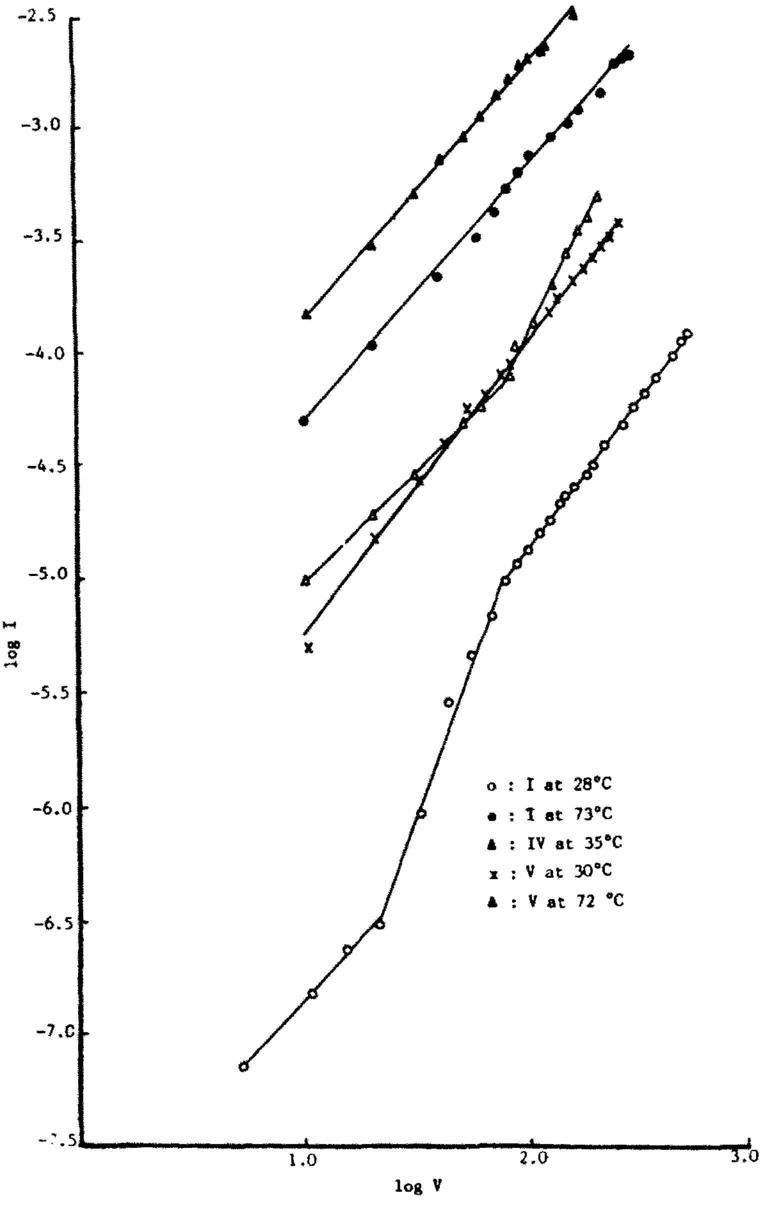


Fig. 4. log *I* versus log *V* for compounds **I**, **IV** and **V**.

duction at 28° C over the applied voltage ranges 5–20, 20–70 and 70–480 V with $n = 1.01$, 2.21 and 1.35, respectively. At 73° C and $V = 10$–290 I, it exhibits only ohmic character. The deduced values for n for the *p*-methoxy derivative (**III**) at 40° C and $V = 10$–50 and 50–440 V are 1.83 and 1.19, respectively. Hence, compound **III** proceeds from SCLC to ohmic conduction. At higher temperature (75° C) the SCLC behaviour extends over the applied voltage range 10–160 V; and at higher voltages a large deviation

TABLE 2

The values of *n* over different ranges of applied voltage and temperature of some derivatives

Compound	Temperature (°C)	Applied voltage (V)	*n*
I	28	5–20	1.01
		20–70	2.21
		70–480	1.35
	73	10–290	1.17
II	35	10–220	1.18
	70	10–240	1.15
III	40	10–50	1.83
		50–440	1.19
	75	10–160	2.00
		160–440	1.46
IV	35	10–80	1.02
		80–210	1.88
V	30	10–240	1.29
	72	10–160	1.06

from ohmic behaviour was observed. It is concluded that the *para* derivatives (**I** and **III**) show I–V characteristics which are temperature dependent.

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