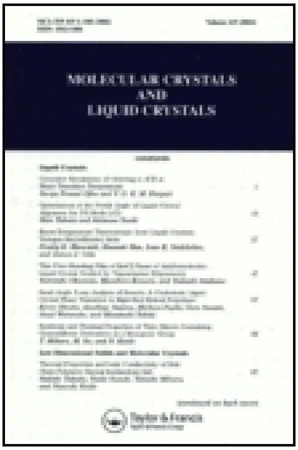

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Electrical Properties of Organic Radical Ion Systems

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Electrical Properties of Organic Radical Ion Systems

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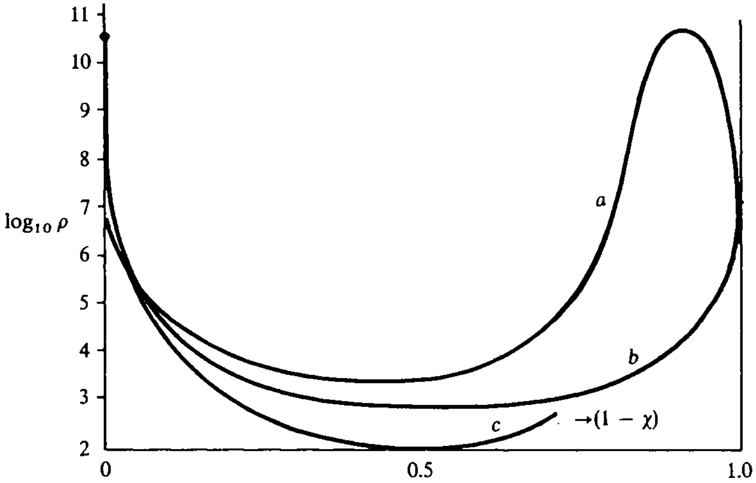
INTRODUCTION

There is a large class of organic compounds which form stable radical ions at room temperature, that is they have a single electron in their highest occupied molecular orbital and carry a negative (e.g. tetracyanoquinodimethane TCNQ) or positive charge (e.g. tetracene tetrasulphide TTS). Many of these compounds are reported as exhibiting semiconductor behaviour with electrical conductivities in the region of 10^0 to 10^{-8} ohm^{-1} cm^{-1}. There is considerable evidence that the electrical conductivity of radical anions such as TCNQ$^-$ is increased by the addition of the non-ionic species from which they are derived.[1] Previously however there has been little evidence to suggest that a similar effect occurs with radical cations although Matsunaga[2] has suggested that the high conductivity of neutral TTS can be accounted for by contamination with the radical cation TTS$^{+\cdot}$. We have shown, in agreement with Inokuchi[3] that freshly sublimed TTS^0 has a low value of conductivity $\sigma_{20} = 10^{-11}$ ohm^{-1} cm^{-1}. Furthermore we have also shown that the conductivity of TTS$^{+\cdot}$ Acetate$^-$ decreases from $\sigma_{20} = 10^{-2}$ ohm^{-1} cm^{-1} to 10^{-6} ohm^{-1} cm^{-1} on careful purification. Apparently the concentration of the different oxidation states of both radical cation and radical anion systems plays an important part in determining their electrical properties. We have, therefore, examined the electrical properties of a number of radical ion systems as a function of the relative concentration of two oxidation states, over the complete range 0% radical cation/100% neutral to 100% radical cation/0% neutral. The results obtained are discussed in terms of a hopping model of conduction and by postulating the existence of a redox equilibrium in the solid state.

RESULTS

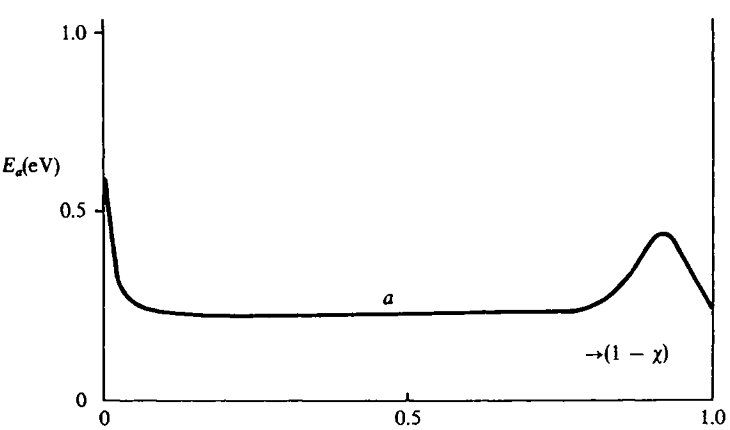
The following results were obtained from a study of the radical cation system derived from 11′Dimethyl 22′ bis(benzthiazolianylidine)azine (Cap–Cap). Qualitatively similar results were obtained from a study of other radical cation systems.

1 *Resistivity vs Concentration of* (· ·)/(+ ·)

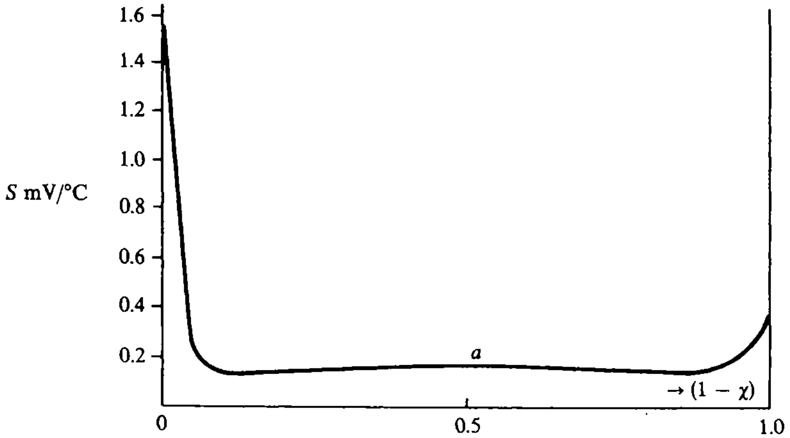


(· ·) = non ionic species
(+ ·) = radical cation
χ = Fraction of (· ·) added to sample
(1 − χ) = Fraction of (+ ·) added to sample.

2 *Activation Energy vs* (1 − χ)



3 *Thermoelectric Power vs* $(1-\chi)$



Curve *a*; Sample prepared by co-crystallisation Curve *b*; Sample prepared by grinding
Curve *c*; Sample prepared by freeze-drying.

DISCUSSION

These results show that the major changes in the measured quantities are confined to the extremes of the concentration range. Thus the addition of ~100 ppm of radical cation in the neutral Cap–Cap species results in an increase in conductivity of 4 decades. Doping the neutral species in this way increases the carrier concentration and substantially reduces the activation energy for conduction with a corresponding reduction in thermopower. Results between 80%–100% radical ion concentration are less reproducible and depend on the method of preparation.

The results can be explained by assuming that charge transport takes place by transfer of electrons from molecule to molecule in a redox process of the type

$$\overset{e}{\overbrace{(\cdot\,\cdot) + (+\,\cdot)}} \longrightarrow (+\,\cdot) + (\cdot\,\cdot) \tag{1}$$

Although not shown each cation is associated with a negative counter ion which does not take part in the conduction process but merely serves to preserve the electroneutrality, unlike the situation in charge transfer complexes. The major effect of the counter ion is to provide an electrostatic potential which influences the energetics of the electron transfer process.

Microscopic examination of the samples shows that freeze drying results in more intimate mixing than grinding but the resulting mixtures are still inhomogeneous. Nevertheless, the better mixing produces a higher conductivity, though it is not clear whether the conduction occurs around or through the crystal grains. Precise analysis of the conduction process is therefore difficult although the general features can be explained. We postulate that a neutral species, capable of forming radical cations, has a very low intrinsic conductivity and that conduction is due to the presence of electronegative impurities which oxidise the host material, forming the radical cation species and thus allowing conduction by the redox reaction described above. If more electronegative material is added the conductivity should rise, and then fall as the radical cation salt is approached since the conduction mechanism requires both the radical cation and the neutral species. However, in some cases the radical cation salt may be quite conducting even when pure if the radical cation disproportionates to the neutral and dication species i.e.

$$2(+\cdot) \rightleftharpoons (\cdot\,\cdot) + (+\,+)$$

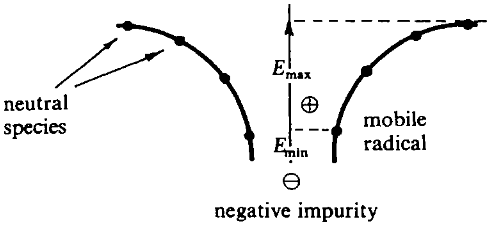
This allows a further conduction mechanism

$$(+\cdot) \overset{e}{\frown} \!\!\!\!\!\!\! + \;(+\,+) \longrightarrow (+\,+) + (+\cdot) \tag{2}$$

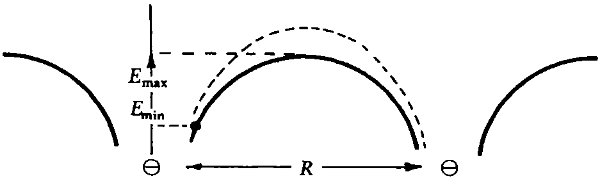
Species with a high equilibrium constant for disproportionation will therefore be expected to exhibit a relatively high conductivity at the composition corresponding to 100% radical cation.

Concentrating upon the doping of the neutral species, the decrease in activation energy and thermopower at doping levels up to a few per cent probably arises from the following mechanism.

Consider the single negative impurity shown below:



The radical cation formed is trapped in the Coulomb well and thus requires activation to E_{max} for d.c. conduction. With increased doping the Coulomb wells overlap and the energy barrier is reduced as shown below:



If the minimum energy corresponds to a separation r_0 between the radical and counter ion,

$$E_{\max} - E_{\min} = \Delta E \sim \frac{e^2}{4\pi\varepsilon_0 \varepsilon}\left\{\frac{1}{r_0} + \frac{1}{R} - \frac{4}{R}\right\}$$

$$\text{i.e.} \qquad \Delta E \sim \frac{e^2}{4\pi\varepsilon_0 \varepsilon r_0}\left\{1 - \frac{3r_0}{R}\right\}$$

This expression yields $\Delta E \sim 1$ eV for r_0 of a few A^0, $\varepsilon \sim 3$ and $R \gg r_0$ and is thus of a reasonable magnitude. ΔE is halved when $R = 6r_0$, which again taking r_0 as a few A^0 corresponds to a radical cation concentration of ~ 1 mole percent for the systems studied, in rough agreement with the observed trends. The constant activation energy over the major region of the graph is thought to be that of the redox reaction itself and is not explained by this mechanism.

At low doping levels the thermopower should merely reflect the activation energy dependence on doping as it obviously does. The positive sign is to be expected for the doped neutral species since the "carrier" is the positive radial cation. It is not obvious why a sign reversal is not observed as the radical salt composition is approached.

This general behaviour is exhibited by several radical cation systems and the complementary behaviour is also seen in radical anion systems. It must be borne in mind, however, that molecular mixing is extremely difficult to achieve, if not impossible, and that all the experimental data is on inhomogeneous samples thus rendering precise theory impossible.

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