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THE INFLUENCE OF TEMPERATURE ON THE INDUCED GAMMA IRRADIATION SEMICONDUCTIVITY OF POLYCRYSTALLINE ACETYLCHOLINE HALIDE ELECTROLYTES

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ABSTRACT

Polycrystalline acetylcholine bromide and iodide samples were purified, recrystallized from the appropriate solvent and well dried under vacuum. Extensive measurements have been made of the d.c. electrical conductivity as a function of temperature and after exposure to an absorbed gamma dose of 5×10^8 rads in air. The results obtained indicated the semiconducting behaviour of the materials investigated in the solid state. Values of the activation energy for conduction, gap width and activation energy for the process of carrier liberation have been estimated, compared and discussed in detail. The effect of gamma absorbed dose damage was found to increase the electrical conductivity values and decrease the activation energy for conduction, i.e. to modify the semiconducting parameters of the materials investigated. Finally, a mechanism was put forward for the first time for gamma absorbed dose induced electric conduction in acetylcholine halide solids.

INTRODUCTION

Radiation can be considered from the point of view of its effect rather than its characteristics. The effects are usually classed as either permanent or transient. Permanent effects are usually attributed to displacements of lattice atoms from their initial equilibrium position at lattice sites. Transient effects are usually attributed to ionization effects in the semiconductor crystals. Thus, Oloff et al. [1] studied the radiation damage in solid single crystalline organic materials and the structure of the investigated materials are discussed in terms of their radio-sensitizing properties. Nagata and Yamaguchi [2] worked on the electronic structure of organic materials containing sulfur, and their protecting action against ionizing radiation. They showed that the

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contribution of *d* orbitals is considered to make sulfur compounds more reactive than other compounds which lack contributions from *d* orbitals. For a number of highly insulating materials [3], the static or dark conductivity may be increased by several orders of magnitude by ionizing radiation. This phenomenon has not hitherto been investigated. The effect of gamma radiation on the electrical conductivity, σ, of 8-hydroxyquinoline metal complexes has been studied by El-Agramy and co-workers [4]. The induced electrical conductivity for the compounds investigated [4] was found to decrease on increasing the energy of the radiation dose, and approaches that of the ligand at doses in the range 300–500 Mrad. On the other hand, the increase of the activation energy, ΔE, by irradiation was found to depend on the crystal field stabilization energy (C.F.S.E.) in a high-spin tetrahedral field and the ionic potential of the metal. An examination has been made of the effect of temperature on the electrical conductivity of a number of crystalline organic powders [5].

But, to date, work has been mainly directed towards the examination of the semiconductivity of organic compounds, a subject of intrinsic interest, and also bearing on many problems of organic reactivity and catalysis by organic compounds. As far as the authors are aware, there is no mention in the literature data concerning either the action of temperature or ionizing radiation on the electrical conductivity of acetylcholine salts in the solid state, which is the major goal of the present investigation.

EXPERIMENTAL

Material preparation

Solid samples of acetylcholine bromide and iodide (supplied from BDH) were purified as well as recrystallized from the appropriate solvent and well dried under vacuum over P_2O_5 for 24 h.

D.c. electrical conductivity measurements

The d.c. electrical conductivity was measured using the two-probe method under vacuum. The circuit used is very similar to that previously described [6]. Measurements were made at room and elevated temperatures up to 430 K and the readings were taken 15 min after each temperature equilibration, before and after a gamma absorbed dose of 5×10^8 rads.

The materials were investigated in the form of compressed pellets (200 kg cm^{-2}) of 12 mm diameter and 2 mm thick. On the two opposite surfaces of each pellet, liquid silver paste was applied in order to give a good contact area throughout the course of measurements.

Gamma radiation exposure

A ^{60}Co gamma cell (500 Curies) was employed and an absorbed dose of 5×10^8 rads was undertaken at room and elevated temperature (up to 430 K) to simulate the conditions performed in conductivity measurements. Measurements were repeated several times and in each case good, reliable data could be obtained.

RESULTS AND DISCUSSION

Measurements of electrical conductivity were undertaken over a selected, relatively moderate temperature range in order to avoid partial oxidation and melting of the materials. Figures 1 and 2 represent the variation of electrical conductivity (log σ) as a function temperature ($1000/T$ K^{-1}) for acetylcholine bromide and iodide before [Fig. 2(A)] and after [Fig. 2(B)] an absorbed gamma dose of 5×10^8 rads. Since there was a positive temperature coefficient of electrical conductivity ($\mathrm{d}\sigma/\mathrm{d}T$) for each curve, all the specimens investigated have semiconducting conduction mechanisms. The conductivity (σ) depends on the concentration of charge carriers (n), their charge (e) and mobility (μ) according to the relation

$$\sigma = ne\mu$$

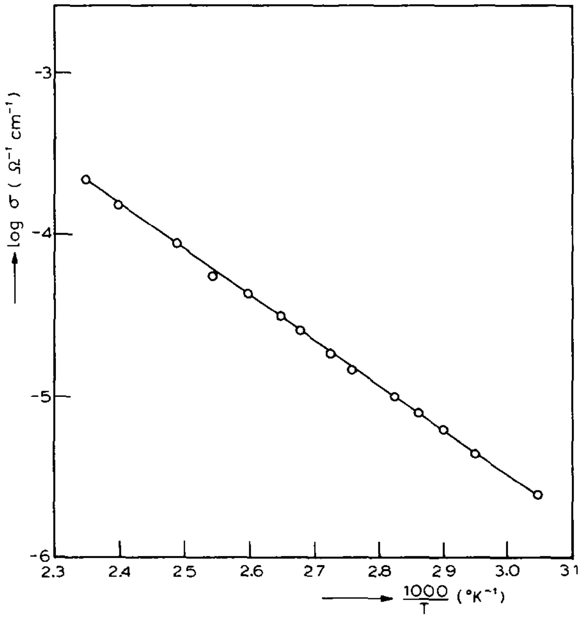

Fig. 1. The values of the electrical conductivity of acetylcholine bromide obtained as a function of temperature.

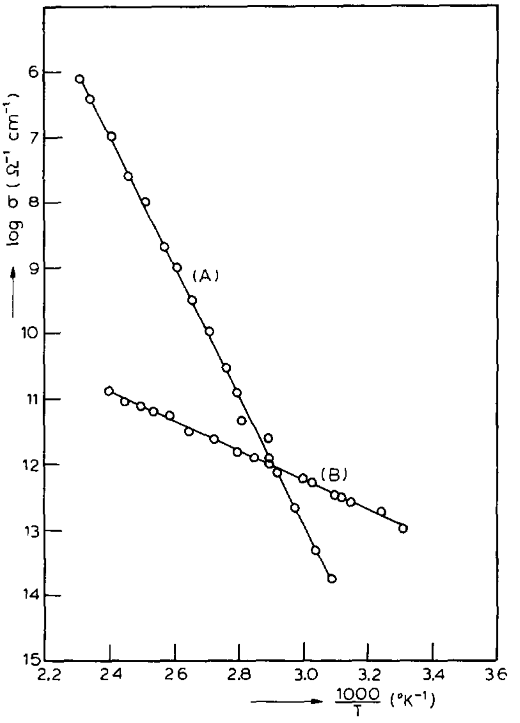

Fig. 2. The variation of electrical conductivity as a function of temperature for acetylcholine iodide. (A) Before irradiation and (B) after irradiation (5.0×10^8 rad).

The concentration of carriers and, hence, the semiconductivity increase with temperature according to a Boltzmann- type distribution with the activation energy (E_A) for the conduction process.

$\sigma = n_0 e \mu \exp^{-E_A/kT}$

Thus, semiconductivity with a positive activation energy, as noted before γ-irradiation, see Fig. 1, curve B, is distinguished from metallic conductivity which falls as the temperature rises.

Mobility is the parameter which has received least attention in studies of the organic compounds. Since these substances showed semiconducting properties with a definite activation energy, E, in the uncompressed state, the activation energy was largely influenced by crystal compacts [7]. Thus, it is suggested that the excited orbitals of π electrons in the isolated molecules overlap to give a non-localized orbital stretching throughout the crystals. As shown in Table 1, $2\Delta E$ is then the energy gap between the highest filled band, or the valence band, and the conduction band. In this respect, its value is discussed in terms of single electron transition in the isolated molecule and overlap of π orbitals between neighbouring molecules. This investigation was originally stimulated by the suggestions of Szent-Gyorgi in an earlier publi-

TABLE 1

Values of the obtained activation energy for conduction and the energy gap for acetylcholine bromide and iodide before (A) and after (B) the radiation dose

Substance	Activation energy E(eV)		Energy gap, $2E$(eV)	
	A	B	A	B
Acetylcholine bromide	0.55		1.10	
Acetylcholine iodide	2.27	0.88	4.54	1.76

cation [8] on the possible role of mobile electrons in protein molecules. From Tables 1 and 2, it can easily be seen that the electrical conductivity decreases and the activation energy increases in going from acetylcholine bromide to acetylcholine iodide. This may be attributed to the existence of ionic association in the case of acetylcholine bromide even in the solid state. This is expected to be more liable to occur in the case of bromide salt than for the iodide, due to the relatively strong ionic bond of the bromide.

However, in a previous work [9] which examined the solution electrical conduction of the same materials investigated here, ionic association in solution was found to act as a hindrance to current flow. This is due to the decreased mobility caused by ionic association. This phenomenon, in solution, appears more pronounced for acetylcholine bromide than for the iodide salt. Accordingly, a link was established for the first time (in the present investigation) that although ionic association appears to decrease the solution conductance, it facilitates electric conduction in solids as it may result in movement of the π electrons to non-localized orbitals which stretch throughout the crystal. This offers an easier way for current flow, resulting in increased values of electrical conductivity in the solid state and its attendant decreased value of activation energy for conduction. The net result is a modification of the semiconducting properties of the materials in the solid state through an ion association mechanism.

TABLE 2

Values of the obtained electrical conductivity, log σ, for acetylcholine bromide and iodide before (A) and after (B) radiation dose

Substance	log $\sigma_{0.0}$		log σ_{25}		log σ_{70}	
	A	B	A	B	A	B
Acetylcholine bromide	−7.30		−6.48		−5.27	
Acetylcholine iodide	−19.35	−13.75	−16.45	−13.05	−12.15	−12.05

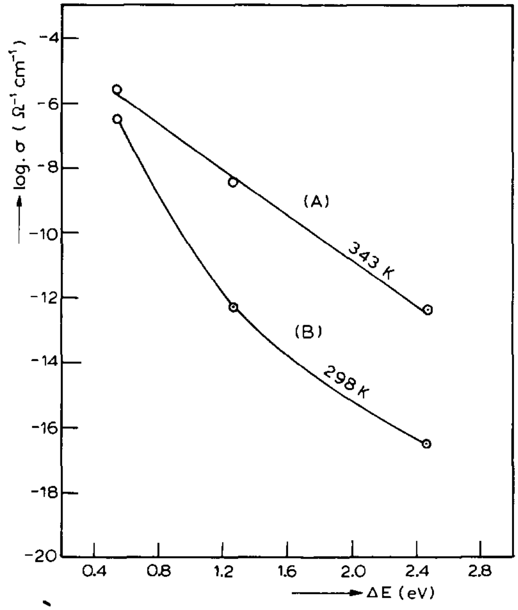

Fig. 3. The correlation between electrical conductivity and activation energy of (A) acetylcholine bromide and (B) acetylcholine iodide.

Figure 3 shows a correlation between electrical conductivity values (log σ_0, σ_{25}, and σ_{70}) and the obtained values of activation energy for conduction of acetylcholine bromide and iodide. At relatively high temperatures a regular straight line relation could be drawn and this is probably explained by the thermally-induced ionic association which takes place more regularly for the bromide salt. This explanation is established practically by the irregular relations which may take place at relatively low temperatures since such low temperatures are insufficient to affect thermally-induced ionic association.

In considering the effect of gamma irradiation, Figs. 2 and 3 curves (B) include the temperature dependence of the electrical conductivity and activation energy for conduction (see Table 2) after the absorbed gamma dose (5×10^8 rads). In this respect, one representative example only is taken for acetylcholine halides, namely the iodide salt. This material was selected since it shows a high response to the absorbed gamma dose (deduced from preliminary tests of IR and X-ray analyses). As a result of the absorbed gamma dose, the electrical conductivity increases and the activation energy for conduction decreases. This could be explained in accordance with the idea that γ irradiation introduces donor centres [10] and/or enhances ionic association in solids. Thus, it can be stated that [11] a gamma absorbed dose causes an increase in the concentration of existing levels or creates new donor levels. Thus, the activation energy for carrier liberation, [12] could be calculated for the material investigated using the relation

$$\phi = \phi_2 - \phi_1$$

where ϕ_2 is the activation energy for conduction after the absorbed gamma dose (5×10^8 rads) and ϕ_1 is the activation energy for conduction before the absorbed gamma dose. Thus, a value of 1.39 eV could be obtained for the activation energy of carrier liberation for acetylcholine iodide.

Accordingly, probable explanation is that the primary radiation damage caused during irradiation is the production of free electrons and point defects (interstitially-located atoms [13] and vacancies) by the absorbed gamma dose (5×10^8 rads). The defects so formed are quite mobile especially at high temperature. The most universal and most important microstructural changes caused by irradiation is the expansion and/or melting of the individual grains or crystallites of the material. This may induce a number of point defects in the normal crystal lattice. Consequently, for the suggested mechanism of absorbed-dose-induced electric conduction in acetylcholine iodide polycrystals, *F* centers [13] are first formed when an electron is captured by an anion vacancy. As a result, there is a decrease in the number of anion vacancies accompanied by a slight increase of conductivity values (as a net result with other contributions). These centres dissociate when heating takes place during conductivity measurements at elevated temperatures and the conductivity of the material is re-established and increases as a function of temperature leading to the observed semiconducting conduction mechanism after the absorbed gamma dose.

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