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E.S.R. Studies on the Semiconductor Theory of Free Electrons in Large Organic Molecules

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I. Introduction.

The work reported in this paper has been performed in order to investigate the plausibility of the « semiconductor theory » of free electrons in proteins. These ideas arose initially from electron resonance studies of different types of melanin [1]. Melanin is a naturally-occuring pigment, but can also be made synthetically, and electron resonance investigations showed that it contained a very high concentration of unpaired electrons, of the order of 10^{17} per cm^3. The fact that these unpaired electrons were directly associated with the melanin itself was also shown by studying melanin which had been artificially bound to protein in varied and known amounts. The measured free radical concentration was found to vary in exactly the same ratios. It was also found that radiation from natural sunlight and from the near ultra-violet produced an increase in the free-radical concentration of melanin-containing tissue whereas irradiation of similar tissue, with no melanin, gave no electron resonance signal. To account for these properties of the melanins, Longuet-Higgins [2] put forward a hypothesis that a non-localized orbital is associated with the whole polymer chain of quinonoid units. If the fully oxidized molecule of a monomer unit has a closed electron shell, then further added electrons will enter the conduction band of non-localized molecular orbitals which is formed by an interaction between the lowest vacant orbitals of the individual quinonoid units. If protons are occasionally added to a unit of such a polymer, it will probably lower the energy of the lowest vacant orbital and thus form an electron trap at the site.

This work on melanin therefore suggested that its behaviour together with that of proteins containing extended polymer units, such as polypeptide chains, might be explained on a « semiconductor » theory with conduction bands formed from non-localized molecular orbitals, and with

« impurity levels », due to protonation, acting as electron traps [3]. In order to test out these ideas we have carried out a series of systematic experiments on the electron resonance spectra observed from proteins irradiated with different U.V. wavelengths. The results so far obtained indicate that additional unpaired electrons are only produced when the energy of the incident radiation is close to that calculated for the forbidden gap in the protein semiconductor. The variation of the signal strengths with temperature also suggests that the electrons responsible for the resonance signal are those that have been excited up to the conduction band, and have then fallen into one of the « traps » formed by protonation of the polypeptide chains.

II. Experimental.

A transmission X-band electron resonance spectrometer with 100 kc/s field modulation, and phase-sensitive detection was used in these experiments. For the low temperature investigations the rectangular cavity was immersed in a bath of liquid oxygen or nitrogen, and the irradiation and resonance measurements were carried out with no intervening increase in temperature. The U.V. irradiation was carried out at either 3560 Å or 2537 Å. The 3650 Å mercury discharge lamp had a 250 watt output concentrated in a small arc, while the other mercury lamp, of 500 watt output, consisted of a spiral tube so arranged that the 2537 Å radiation was concentrated into the specimen tube. In this case the sample was placed between the spiral source and a parabolic reflecting mirror with an aluminized front surface so that it would receive the maximum amount of irradiation. Throughout the experiment clear silica sample tubes were used, and when the specimen was to be irradiated at low temperatures it was placed in a clear quartz dewar containing liquid nitrogen.

III. Results.

Figure 1 shows the spectra that are obtained after irradiation of tyrosine, leucine and egg albumin, with a wavelength of 3650 Å at 77° K. It is evident that no definite signal is obtained when the simple amino acids are irradiated in this way, but the egg albumin shows quite a large resonance absorption. This signal is found to disappear completely on warming the sample to room temperature, showing that it is not due to permanent damage of the molecule. On the other hand, such irradiation damage is

produced in all of the specimens if they are irradiated with the higher energy 2537 Å wavelength, and this signal remains undiminished on warming to room temperature.

It was also found that the disappearance of the signal from the egg albumin, on warming, was very sensitive to the exact nature of the specimen.

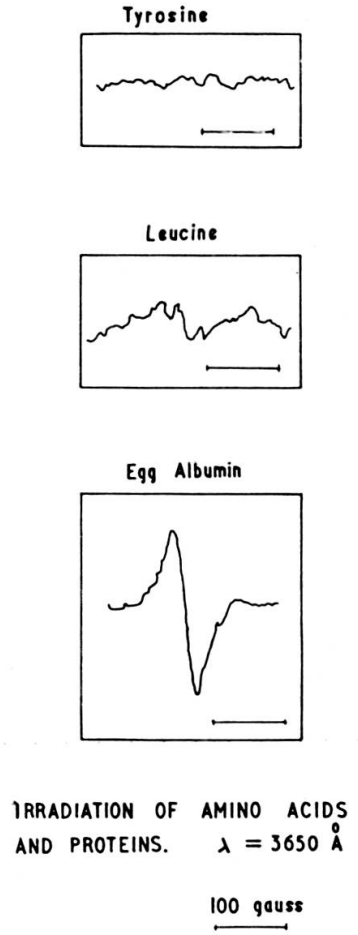

Fig. 1.

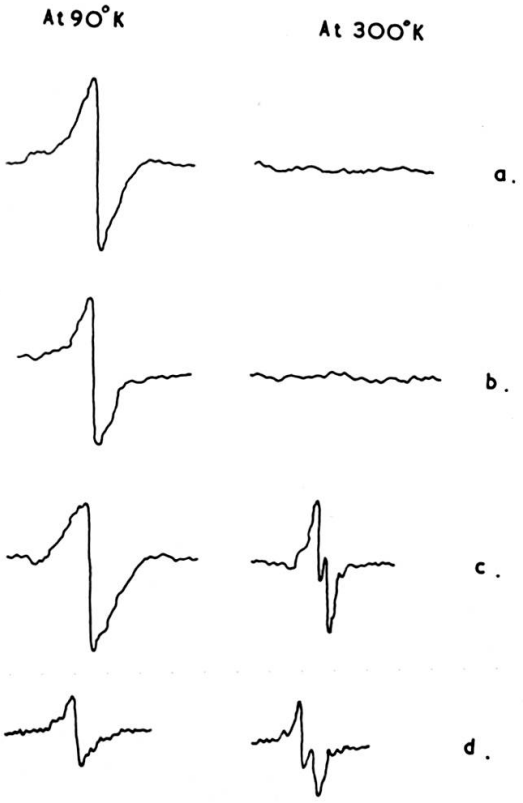

Fig. 2.

Thus if the sample consists of protein dissolved in water in its normal form, or is in an untreated polycrystalline form, then the absorption is found to disappear completely on warming, as shown in figures 2 *(a)* and *(b)*. If, however, the polycrystalline sample is evacuated before deep-freezing and irradiation, or the crystals are suspended in alcohol instead of aqueous solution, then the signal does not disappear on warming, but becomes a well-resolved doublet, as shown in figures 2 *(c)* and *(d)*. It would therefore appear that the presence of loosely bound water, as it occurs in its normal

environment, is necessary for the energy level system of the protein to act as a semiconductor.

These measurements have been repeated with other proteins and the general results outlined above have been confirmed. As a preliminary hypothesis it would appear that only globular proteins with a coiled polypeptide-chain system can form a definite set of semiconductor energy-level systems with the low-lying traps; and that these systems are radically upset by treatment with alcohol, or any other denaturising process.

IV. Discussion.

The ability of electrons to exhibit mobility in biological systems is of widespread interest. In 1941 Szent-Gyorgyi [3], in order to explain many biochemical reactions involving energy transfer, postulated the existence of common energy bands existing over a complete molecule. He arrived at this conclusion also in view of the regularity of protein structure. In 1949 Evans and Gergely [4] gave this hypothesis a mathematical basis and actually calculated values for the forbidden gap, and width of the bands that might exist in a protein semi-conductor. Recently experimental work has been performed that supports this calculation. Eley et al [5] have measured the forbidden gap in several proteins; their value of 3 eV corresponding closely to the calculated value of 3.2 eV. It should be noted in this connection that the U.V. absorption at 3,600 Å is equivalent to an energy of 3.4 eV.

The results of our own measurements seem to be definite confirmation of the « semi-conductor theory » of electrons in large protein molecules. The most straightforward interpretation of the results on the egg albumin is that the electrons are being excited into the upper conduction band by the 3650 Å irradiation, and some of these are then falling into low-lying traps formed by the presence of odd protons along the polypeptide chain system. On warming to room temperature, these trapped electrons are re-excited to the conduction band, and then return to the ground state, so that the resonance signal disappears.

The change in the room-temperature spectra that occurs when the protein structure is interfered with can then be explained by the formation of deeper traps, or defects, in the general structure, into which the re-excited electrons may fall. The resolved doublet structure of these may then be evidence for strong hydrogen bonding at such sites. This conclusion that

interference with loosely bound water molecules attached to the protein radically alters the semi-conductor band system is in line with recent ideas on the importance of « ordered structure » in the water molecules which are associated with bio-physical systems.

It is also of interest that the production of excitons in such a banded system has many biological implications, such as their possible interaction with carcinogenic hydrocarbons as recently postulated by Mason [6].

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