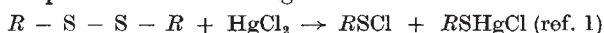


the weakening is brought about by the fission of strained disulphide bonds according to the reaction:



This view is supported by the higher extension at break of fibres stretched in the mercuric chloride solution, as well as by the general similarity between these results and those obtained with fibres which were stretched in presence of adsorbed iodine². In both cases the break-down occurs mainly in those regions of the fibre which give the higher modulus of the third part of the load/extension curve.

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BIOCHEMISTRY

Examination of Optically Excited Amino-acids by Electron Spin Resonance at Very Low Temperature

WE have recently¹ investigated the irradiation by ultra-violet light of amino-acids at low temperature. Preliminary results of an investigation by electron spin resonance were given. We mentioned the difficulties of a correct interpretation of the signals obtained on micro-crystalline powders of phenylalanine and tryptophan. Here are the first results of an investigation concerning solutions of aromatic amino-acids (tryptophan, phenylalanine, tyrosine).

At low temperatures transparent glasses are obtained with certain solvents. The purified and degassed samples are directly irradiated in the cavity of a Varian 4502 O2 spectrometer at the liquid nitrogen temperature. The source of light is an Osram HBO 200 lamp without filter. There is a great difficulty in obtaining sufficiently concentrated solutions as the solubility of these amino-acids in ether-pentane-alcohol (EPA) is very low. But it can be raised by addition of alcohol and thus it is possible to obtain an electron spin resonance signal with tryptophan for $g \approx 2$ after a few minutes of irradiation.

But the following results show that the signal is not specific of the solute because there is certainly a photosensibilization of the alcoholic part of the solution. Alcohols alone give better solubility (10^{-2} M with methanol, ethanol). Great care must be taken in avoiding crystallization. Two kinds of electron spin resonance signals are then obtained.

Electron spin resonance signals of the triplet state of phenylalanine, tyrosine and tryptophan. We know² that it is possible to induce a resonance transition corresponding to $\Delta m = 2$ in several organic molecules; Smaller succeeded

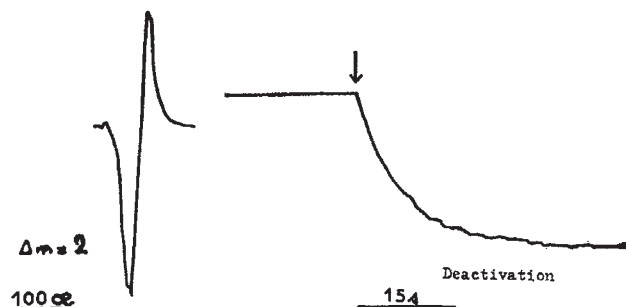


Fig. 1. Triplet state of tryptophan in methanol at low temperature

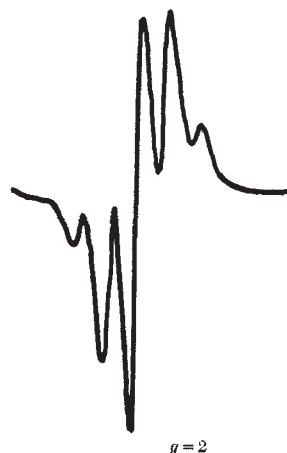


Fig. 2. Electron spin resonance signal of photosensitized methanol

in investigating the triplet state of indole³ and benzene⁴ by electron spin resonance.

With these three amino-acids in alcoholic solution, at low temperature, we obtained signals which are specific of the state $S = 1$ (Fig. 1). Their form, position and deactivation kinetics are characteristic of the molecule considered. More information will be available with the complete calculation of the spin Hamiltonian.

Electron spin resonance signals of free radicals produced with solvents. For the normal transition $\Delta m = 1$, intense signals are obtained, and if we investigate their structure we can make the following conclusion: for sufficient concentrations of amino-acids we observe the photosensibilization of the alcohols by appearance of free radicals (Fig. 2).

The nature of these radicals, their appearance kinetics, their development with temperature are quite complex⁵. In the first seconds of irradiation we have a rather weak signal, similar to that of the methoxy CH_3O radical. Then it grows notably in intensity and complexity, giving a signal which must be that of the CH_2OH and CHO radicals. Smaller observed similar reactions with indole solutions in methanol.

In conclusion, it is difficult to make out the existence of radical configurations in amino-acids by electron spin resonance. With new experimental conditions we might be able to obtain a characteristic electron spin resonance signal of the solute and to give its right interpretation.

Recent results of Gill and Weissbluth⁶ on the thermoluminescence of polycrystalline samples of amino-acids induced these authors to admit the existence of such metastable configurations. But the results obtained in the same time by electron spin resonance are much more delicate to analyse. This conclusion and our observation of a triplet state pose the problem of the relationship between the triplet and the metastable states of the molecules of aromatic amino-acids: we are now investigating this matter.

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