free-radical chain reaction propagated by radicals of low reactivity[3].

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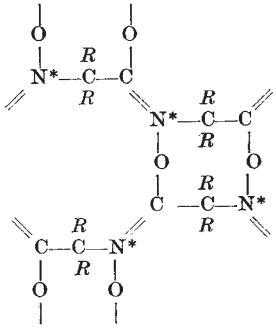
Possibility of Ionic Dissociation at the Peptide Linkage

THE need for a cyclic structure for certain proteins (for example, serum globulins) has been emphasized in a series of papers by Wrinch[1,2]. However, the hexacyclic carbon–nitrogen ring structure which she proposes has not been generally accepted, due partly to steric objections. It is believed at present that two-dimensional protein structures are formed by hydrogen bonding between polypeptide chains. In the present communication a new oxygen cross-bonded structure is suggested. It is characterized by ionic dissociation, and a double bond, at the peptide linkage. The structure is:



where N* is either N^- or $(HNH)^+$ depending on whether the dissociation:

$$NH \rightarrow N^- + H^+ \qquad \text{(acidic)}$$

or

$$NH + H^+ \rightarrow NH_2^+ \qquad \text{(basic)}$$

occurs. The amino-acid residues (*R* groups) and the H ions of $(HNH)^+$ groups lie perpendicularly to the plane of the structure.

The reason why both acidic and basic dissociations are thought to be possible is as follows. In the above structure, N atoms complete their $n = 2$ shell octet by sharing 4 of their 5 valence electrons in covalent bonds with neighbouring atoms. The fifth valence electron is therefore forced up into a 3*s* level where it will behave very much like the 3*s* valence electron of sodium. One knows that sodium hydride dissociates into Na^+ and H^- ions (the latter combining with H^+ ions of water to give H_2) and consequently one might expect that NH would dissociate similarly. This is essentially the basic dissociation shown above. However, the 3*s* electron of the N will be more tightly bound than the 3*s* electron of Na when the adjacent amino-acid residues are electrophilic (electron deficient), because then the covalent bonds to the N atom will tend to be polar, causing the N charge to exceed by a slight amount one electron charge. In this case acidic dissociation of NH may be expected. The dependence of the type of dissociation on the electrophilic or nucleophilic character of adjacent amino-acid residues means that the genetical code of a protein residing in its sequence of amino-acids can be transferred to a sequence of ionic charges at the peptide linkages.

The delicate balance between acidic and basic dissociation at the peptide linkage will mean that the free energy of dissociation is exceptionally small. One therefore expects proteins to be precipitated by slight changes to the solvent. It is well known that slight changes of *p*H and reagents such as methanol do, unaccountably, precipitate protein. One may expect also a tendency of positively charged ions of the correct electronegativity to complex with N^- ions at the peptide linkage. This may explain the denaturation of proteins by heavy ions in solution, and possibly also the different response of biological organisms to the chemically similar Na^+ and K^+ ions and the chemically similar Ca^{2+} and Mg^{2+} ions.

A definite need to invoke new dissociations has been found in the case of the proteins of tobacco mosaic virus[3] and in the case of silk fibroins[4]. The net charge of these proteins indicated by electrophoretic measurements differs considerably from that deduced from chemical analysis (for the same *p*H). Furthermore the *p*H of minimum movement under an electric field (the true isoelectric point by definition) differs from the *p*H of minimum combination with acid or alkali (often termed the isoionic point).

Preliminary experiments I have made show that ultra-violet irradiation can alter the net charge of serum protein. Part of a protein front moving along an electrophoretic strip in a buffer of *p*H 8·6 was made to pass through a narrow band of ultra-violet radiation. In the case of negatively charged protein (albumins) the ultra-violet irradiation produced an acceleration, while in the case of positively charged protein (γ-globulins) a retardation was noted. It would seem that the ultra-violet irradiation tended to increase the net negative charge of the protein by destroying positive charges. Since it is reasonable to assume that the ultra-violet irradiation is absorbed at a double bond, this appears to constitute evidence for ionic dissociation at the peptide linkage.

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