

After completing the preliminary work described in this report, our attention was directed to the work of Walton-Smith *et al.*² on the preservation of timber, using copper formate. These workers have concluded from indirect evidence that, after impregnating the wood with copper formate followed by autoclaving, the copper is converted to a copper-cellulose complex and that it is this complex which confers upon the wood its durability. Our own results prove conclusively the existence of the complex, and, taking their results with ours, we can be rather specific concerning the location of this copper within the cellulose microfibrils.

Cellulose microfibrils consist of a number of molecular chains of cellulose lying parallel to each other and, over certain regions of the microfibril, regularly arranged in a space lattice. It is quite impossible to conceive that aqueous solutions containing copper ions could penetrate into these crystalline regions since water itself is known not to penetrate. These regions, however, are surrounded by others in which the cellulose is paracrystalline; the cellulose chains here lie approximately parallel to each other but are not regularly spaced. Within these regions the copper ions can penetrate, and it is in these areas of the microfibrils that we would expect the copper-cellulose complex to form.

Walton-Smith *et al.*² have found that the maximum amount of copper fixed within the wood using their

copper formate method is about 0.8 per cent by weight of copper. This copper loading corresponds very roughly to 1 copper atom per 20 glucose residues within the paracrystalline regions of the microfibrils. It is clear that if this copper were distributed uniformly within the paracrystalline regions, a uniform space lattice would not develop and no electron diffraction diagrams of the copper-cellulose complex would be possible. The fact that electron diffraction diagrams are obtained shows quite clearly that the copper is located within the paracrystalline regions of the microfibrils, and within these regions sufficient copper is incorporated to link the cellulose chains laterally into an ordered space lattice.

We conclude, therefore, that the metallic components of a copper-chrome-arsenic water-borne preservative impregnated into Douglas fir are located within the cell wall. A proportion at least of this metal complexes with the cellulose of the paracrystalline regions of the microfibrils and the resulting metal-cellulose complex is highly orientated. We are not yet certain as to any connexion with this complex of the crystalline deposits observed in the electron microscope to be distributed at random within the walls.

¹ Trocus, C., and Hess, K., *Z. phys. Chem.*, **6**, No. 1, 1 (1929).

² Walton-Smith, F. G., Bottoms, R. R., Abrams, E., and Miller, S. M., *Forest Prod. J.*, **6**, No. 9, 340 (1956).

PHOTOSYNTHESIS

A SYMPOSIUM on photosynthesis occupied the morning session, on September 10, of Section K (Botany) during the recent Dublin meeting of the British Association. Prof. W. Stiles was in the chair.

Dr. G. E. Fogg, of University College, London, opened the symposium with a paper on "Actual and Potential Yields in Photosynthesis". He said that the total energy reaching the Earth's surface was 5×10^{22} calories a year; at present the most effective conversion of this to potential energy is by green plants in photosynthesis. Schroeder's estimate of the total yield of photosynthesis on Earth, particularly of the yield of forests, namely, 1.63×10^{10} tons of carbon per year, was probably too small. An estimate of the forest production based on the most recent information was 1.54×10^{10} tons per year (instead of 1.10×10^{10}), giving a revised total world production of 2.1×10^{10} (or 2.4×10^{10} if respiratory losses were allowed for). There is still uncertainty as to the total production in the oceans. Using the radiocarbon method, Steemann Nielsen recently found an average value for tropical and sub-tropical waters of between 0.1 and 0.2 gm. carbon/m.²/day. Other workers have found somewhat higher values, suggesting a total production for the whole hydrosphere of 3.2×10^{10} tons per year. This is considerably less than some earlier estimates. One difficulty is to decide whether the radiocarbon method measures net or gross production: further error will arise if any of the products of photosynthesis are excreted from the plant. The value of 3.2×10^{10} is to be regarded as a firm lower limit and in fact may be too small by a factor of up to five.

If the radiation of utilizable wave-lengths alone is considered, then a total yearly production of 5.6×10^{10} tons corresponds to an efficiency of energy conversion over the Earth's surface as a whole of approximately 0.2 per cent. Under optimal conditions of low light intensity in the laboratory, efficiencies of 25 per cent and greater have been obtained. In part, the efficiency in the field is lower because the intensity of sunlight is too high for efficient conversion by the plant. To obtain higher values under natural conditions it is necessary to find new varieties or new crop plants which are capable of utilizing efficiently the natural radiation and then seek methods of using their produce. An ideal crop plant would have a complete ground-cover throughout the growing season, continuously producing new leaves and allowing a continual harvesting of leaves after they had passed their maximum activity. Alternatively, unicellular algae offer the possibility of higher yields, but these must be grown in tanks specially designed to obtain maximal utilization of light energy. In this case, sewage can be used as a source of carbon dioxide. Yields up to 34 gm. carbon/m.²/day have been obtained in small-scale trials. The price of the product is likely to be five to ten times that of conventional crops, and Dr. Fogg concluded that the process is unlikely to be economically possible in the near future unless some radical simplification in technique is achieved.

Dr. C. P. Whittingham, of the Botany School, University of Cambridge, spoke next on "The Chemical Nature of Photosynthesis". He began by discussing the work of Calvin and his colleagues who, by combining the techniques of paper chromatography

graphy and tracer carbon, were able to make great advances in our knowledge of the biochemistry of photosynthesis. Two types of experiment gave information as to the intermediates between carbon dioxide and carbohydrate. First, the percentage activity of a compound as a fraction of the total radioactivity fixed was determined, and the first-formed intermediate assumed to be that which, at zero time, would extrapolate to 100 per cent. This type of experiment indicated that phosphoglyceric acid was the compound first formed from carbon dioxide. Secondly, evidence was obtained by determining the relative activity of individual carbon atoms in the labelled molecules. The first-formed phosphoglyceric acid and hexose were labelled exclusively in the third and the third and fourth carbon atoms, respectively, indicating a two-carbon precursor. In fact, the two-carbon compound postulated turned out to be a five-carbon molecule, ribulose diphosphate. In light, phosphoglyceric acid is believed to be reduced to triose and hence to carbohydrate; in addition, some triose and hexose are converted via sedoheptulose to re-form more ribulose, which then continues the reaction sequence. A continuous supply of two reagents is required to operate the cycle in the direction of net synthesis: a supply of reducing power and of adenosine triphosphate. Both must be produced as a result of the absorption of light energy.

Previous to work with carbon isotopes, a physical separation of the process of carbon reduction from that of the fixation of light energy had been achieved by Hill using chloroplasts isolated from the plant. As then prepared, isolated chloroplasts showed no reaction with carbon dioxide, but were able, in light, to reduce ferric salts, quinone and other substances. It is possible that in the plant, reoxidation of part of the reduced product via a suitable enzyme system could result in the formation of adenosine triphosphate, thus supplying both requirements of the carbon cycle. Dr. Whittingham suggested that those cytochromes which are known to occur only in photosynthetic tissues might be concerned in this phosphorylation which depends on light. Isolated chloroplasts, suitably prepared, have more recently been shown both to phosphorylate suitable acceptors in the light and to be also capable of carbon dioxide reduction. Thus any spatial separation of the photochemical and thermochemical processes in photosynthesis is not at the gross morphological level of plastid and cytoplasm.

Attempts have recently been made to study the structure of the chloroplast and relate it to its photochemical activity. The electron microscope has revealed a multi-layered structure with areas of a high degree of organization, tentatively identified with the 'grana' seen in the light microscope. Mercer and his colleagues in Australia have studied the change in structure occurring during greening of etiolated maize seedlings. In the etiolated plant the chloroplasts had an irregular granular appearance, but as greening occurred the development and organization of a layered structure were observed concomitant with the development of photosynthetic activity. The extensive interfacial area produced by a multi-layered structure offers a surface suitable for the orientation of chlorophyll molecules. This would result in a concentration of pigment within the interface, thus facilitating energy transfer both between accessory pigment molecules and between chlorophyll

molecules. Tentative calculations show a permissible transfer of excitation energy from an absorbing molecule through several hundred other molecules before dissipation. Long ago, Emerson and Arnold showed that not every chlorophyll molecule, but about only one in every five hundred, was capable of producing oxygen from a brief intense light flash. This would be consistent with a unit of 500-1,000 chlorophyll molecules associated with each energy conversion centre. Such a unit is much smaller than the chloroplast or the granum and might be identified with a portion of lamellar interface. The nature of the energy conversion centre at which excitation energy is converted to chemical bond energy is still not clear. Some consider it to be an enzymic link between intermediates of the carbon path and certain individual chlorophyll molecules. Others favour the view that it is a physical structure with polar character analogous to a *p-n* junction. Excitation results in a supply of electrons to one surface and depletion from the other; the electrons and 'positive holes' then initiate respectively the carbon reduction process and oxidation of water to molecular oxygen.

The final paper was by Dr. S. R. Elsdon, University of Sheffield, who spoke on "The Photosynthetic Bacteria". Photosynthesis in all three major groups, the Chlorobacteriaceae, the Thiobacteriaceae and Athiorhodaceae, differs from that in the green plant in that no oxygen is produced and an additional substrate—more or less specific to the group—is required. Nevertheless, there are a number of features common to photosynthesis in bacteria and the green plant.

All three groups of bacteria contain both chlorophyll and carotenoid pigments and these are located in small spherical particles, the chromatophores. The chlorophyll of the Chlorobacteriaceae appears to be very closely related to the chlorophyll *a* of the green plant; the Thiobacteriaceae and Athiorhodaceae have a different chlorophyll which is a tetrahydroporphin derivative. The action spectra for growth and for photosynthesis are similar to the *in vivo* absorption spectrum of the chlorophylls, indicating that the chlorophylls are the primary photosynthetic pigments as in green plants.

The Thiobacteriaceae can use as substrate hydrogen, sulphur compounds and a wide range of organic compounds; the Athiorhodaceae can use hydrogen and organic compounds but not sulphur compounds. With organic substrates most of the substrate carbon is converted to cell substance, but in addition carbon dioxide is taken up if the substrate is more reduced than carbohydrate and given out if more oxidized. This has made it difficult to determine the amount of carbon dioxide fixation. Attempts to use carbon-14 dioxide have been complicated, due to the presence of exchange reactions. Inhibition by cyanide is greater where a substrate is metabolized with the fixation of more carbon dioxide. It appears probable that the process of carbon dioxide fixation in the bacteria is similar to that in the green plant.

Specific cytochromes have been found in the photosynthetic bacteria and are presumed to play a similar part to that of the cytochromes found associated with the chloroplast of the green plant. The bacterial cytochromes are of the *c* class with absorption maxima for the α -band between 550-555 m μ . They are not autooxidizable and differ in oxidation-reduction potential from organism to organism, varying, for example, from -100 mV for

a compound isolated from the green bacterium *Chlorobium thiosulphatophilum* to +340 mV. for a compound from *Rhodospirillum rubrum*. Duysens and Chance and Smith have shown by studies of difference spectra that a haem pigment is relatively oxidized in light and reduced in dark in *Rhodospirillum rubrum*. Illumination of preparations of chromatophores isolated from the bacterium is accompanied by phosphorylation of adenosine phosphate, and it is probable that this is related to the oxidation of haem pigment observed in light. This would indicate a close similarity in the photochemical activity of chloroplasts isolated from the green plant and chromatophores isolated from the photosynthetic bacteria.

The elucidation of the reactions involving carbon dioxide using isotopes and the comparative studies of photosynthesis in bacteria and green plants emphasize that the basic biochemical pattern is essentially similar to that of the dark metabolism of other organisms, both plant and animal. The unique feature of photosynthesis lies in the mechanism whereby light energy is used to drive the reaction sequence in the direction of net synthesis. An understanding of the mechanism of energy conversion is the major challenge for future research in photosynthesis and may contribute to the technology of energy conversion just as the study of the over-all process of photosynthesis has to the technology of food production.

C. P. WHITTINGHAM

A TRIBUTE TO FREDERICK SODDY*

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THE first International Conference on Radioisotopes in Scientific Research seems an appropriate occasion upon which to consider our debt to Frederick Soddy. The duty to clarify his picture is specially incumbent on us, as it is the tragedy of his life that members of the younger generation may know him only as the person who adopted the term 'isotope' and, perhaps, as the author of provocative statements in economics and other fields far remote from science. The number of those who knew Soddy in his creative period is dwindling.

In fact, the whole science of radioactivity owes to Soddy infinitely more than the coining of the household word which is the unifying tie of this Conference.

First, I would like to recall that the fundamental theory of radioactive disintegration was developed by Rutherford and Soddy. From experiments carried out during 1901-3 at the University of Montreal by the physicist Rutherford and the chemist Soddy, they drew the conclusion that the emission of the Becquerel-rays (as they were called in those days) was accompanied by chemical transmutations; in a vague way such a hypothesis had been considered before as one of several possibilities, but the French school in particular had favoured other explanations. Anybody who studies the original papers will easily recognize the decisive part the chemist must have played in this joint work; some of the arrangements are, from the point of view of experimental chemistry, models of a scientific investigation. Nevertheless, in later books Soddy's name sometimes no longer appears in this context: to Rutherford is attributed the sole merit—illustrating the old truth, well known to students of the history of science, that great reputations tend to absorb the smaller ones—although Rutherford himself always gave full credit to his colleague.

Their ways, however, soon parted. Soddy's name immediately appeared again in connexion with an experiment of the greatest significance: the proof that, in the process of radioactive disintegration by α -rays, helium is evolved in sufficient quantities to be identified spectroscopically. This time the team was Ramsay and Soddy: the study of such small

quantities of rare gases is so difficult that in those days Ramsay's laboratory in London was the only place where the necessary experience was available, but the radioactive technique—then quite new to Ramsay—was clearly Soddy's contribution. Anybody who knows from Ramsay's later publications on radioactive transmutation, after Soddy had left, how incapable he was of taking the precautions necessary in this field will credit Soddy with the clean and convincing conduct of experiments in which he later proved himself so much more adept than Ramsay.

So far, Soddy's name had been linked with those of senior and already very famous investigators. He came fully into his own during the ten-year tenure of a lectureship in physical chemistry at the University of Glasgow, where he devoted himself to radiochemistry proper, that is, to the study of the chemical behaviour of the radioactive substances. Such work had been going on in many laboratories, but the published results were frequently erroneous and no attempt had been made at a comprehensive survey. By far the clearest presentation of the new subject was given by Soddy in 1911, in a small volume called "The Chemistry of the Radioelements". Here, for the first time, the phenomenon of the chemical inseparability of those substances which to-day we call isotopic was stressed as something fundamentally new and important. More than that, a connexion was indicated between the position that a radioelement occupies in the disintegration series and in the periodic table; the first part of the important 'radioactive displacement law' is already contained in this book, namely, the rule that emission of an α -particle means shifting down by two places in the periodic table. The second part of the law, namely, that emission of a β -particle leads to the production of an element one place higher in the table, was pronounced three years later, almost simultaneously, by Fajans and Soddy; the experimental basis for this statement had in the meantime been safely laid, largely through the systematic efforts of Soddy's laboratory. In the course of various researches the inseparability of some radioelements from other elements had independently been found by Svedberg, by Boltwood, by Hahn and others, but it is Soddy's outstanding merit to have undertaken a special

* Address delivered in Paris on September 9 at the inaugural session of the International Conference on Radioisotopes in Scientific Research.