

CX.—*Photocatalysis. Part I. The Synthesis of Formaldehyde and Carbohydrates from Carbon Dioxide and Water.*

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THE photosynthesis of carbohydrates in the living plant unquestionably forms one of the most interesting problems in chemistry, and up to the present it has been very far from being understood. Many experimental results have been published, but no very definite conclusions can be drawn from them. Thus it does not seem definitely to have been established whether or no formaldehyde is actually the first stage in the synthetic process, assuming, of course, that the initial materials are carbon dioxide and water. One of the difficulties met with is the absence of proof that formaldehyde exists in growing leaves as a definite intermediate stage. There is no doubt that the general concensus of opinion is in favour of the view that formaldehyde is photochemically synthesised from carbon dioxide and water, although theories differ as to the chemistry of the process, and that the formaldehyde is then polymerised to form carbohydrates.

On the other hand, Moore and Webster (*Proc. Roy. Soc.*, 1914, [B], 87, 163, 556; 1918, [B], 90, 168) seem to take the view that formaldehyde does not form one of the stages in the photosynthesis of carbohydrates, because they say that, if formaldehyde were formed, it would combine to form stable complexes with the proteins, and this would prevent its polymerisation to form sugars. This opinion is somewhat striking in the light of the experimental evidence published by these authors. They have undoubtedly proved (1) that formaldehyde is formed by the action of ultra-violet light on carbon dioxide and water in the presence of certain inorganic "catalysts," and (2) that formaldehyde is polymerised to reducing sugars in ultra-violet light. Clearly, therefore, carbohydrates can be synthesised from carbon dioxide and water under certain conditions in two stages. On the other hand, Moore and Webster have found that chlorophyll and all organic substances of biochemical origin give formaldehyde on exposure to ultra-violet light, and thus it would seem that the photosynthesis of biochemical substances from formaldehyde does not take place in the plant. Moore and Webster's results are therefore, in a sense, contradictory, and their evidence does not seem to bring the problem very much nearer solution.

We have made a number of experiments on photosynthesis, and as the result of these are able to state that it is possible to synthesise carbohydrates from carbon dioxide and water in light and that formaldehyde does form the first stage in the photosynthetic process. It is well known that carbon dioxide absorbs ultra-violet light of very short wave-length ($\lambda = 200\mu\mu$), and that formaldehyde absorbs ultra-violet light of longer wave-length ($\lambda = 290\mu\mu$). Hence, the ultra-violet light which will act on an aqueous solution of carbon dioxide has a much shorter wave-length than that which will act on an aqueous solution of formaldehyde, and if the photosynthesis of the carbohydrates from carbon dioxide and water takes place in two stages (formaldehyde formation and subsequent polymerisation), light of two different wave-lengths will be required.

The first point to be proved was whether an aqueous solution of carbon dioxide gives formaldehyde on exposure to light of very short wave-length. Moore and Webster state that no formaldehyde is formed, but this statement is incorrect. It is perfectly true that if water saturated with carbon dioxide is exposed in quartz vessels to sunlight or the light from the quartz mercury lamp, no formaldehyde is to be found in the solution. If, however, during the exposure carbon dioxide is passed through the water, very definite evidence is obtained of the formation of formaldehyde. The explanation of Moore and Webster's failure to discover formaldehyde is to be found in the fact that when the solution of carbon dioxide is not agitated the formaldehyde produced is polymerised to carbohydrates as fast as it is formed. When the solution is agitated, some of the formaldehyde is carried to the back of the quartz vessel, where it is more protected from the light. A small amount therefore escapes polymerisation, and this can very readily be detected by Schryver's test. We have further found that when the carbonic acid solution is exposed in thin glass vessels to the light, no formaldehyde is produced, which clearly proves that the effective light has a very short wave-length.

We have also investigated the effect of ultra-violet light on aqueous solutions of formaldehyde, and find, as did Moore and Webster, that polymerisation to active or reducing sugars readily takes place. Moreover, if the formaldehyde solutions are exposed in thin glass vessels, the polymerisation still takes place, although much more slowly. It is thus evident that the effective light has a greater wave-length than that required for the synthesis of formaldehyde from carbon dioxide and water, so that if a solution of carbonic acid be exposed to ultra-violet light and protected from those specific rays which cause the polymerisation, the amount of form-

aldehyde formed in the solution will be increased. It is quite possible to find a solution which selectively absorbs these rays while being transparent to the very short wave-length rays. If such a substance does not interfere in any chemical sense, it may be added to the water through which the carbon dioxide is being passed. We find that paraldehyde fulfils these conditions. A solution of paraldehyde in CO_2 -free water gives no formaldehyde on exposure to light, and a solution of formaldehyde containing paraldehyde is stable to light, that is to say, the paraldehyde completely protects the formaldehyde from those rays which cause its polymerisation. We then found that an aqueous solution of paraldehyde containing carbon dioxide gives a very good yield of formaldehyde on exposure to the light from the quartz lamp. The paraldehyde does not act as a catalyst in the formation of formaldehyde, but merely as a protector of the formaldehyde when formed. An exactly similar result is obtained with sodium phenoxide. In the absence of carbon dioxide, no formaldehyde is formed, a solution of formaldehyde is not polymerised by light in the presence of sodium phenoxide, but a solution of sodium phenoxide in the presence of carbon dioxide on exposure to ultra-violet light gives a good yield of formaldehyde.

Exactly the same explanation applies to the metallic salts, ferric chloride, uranium nitrate, etc., which Moore and Webster say are "catalysts," for it appears that they do not catalyse the production of formaldehyde, but merely protect it when formed. We have proved this by direct observation of the stability of formaldehyde solutions containing these "catalysts" on exposure to light, and have confirmed it by light absorption experiments which establish the fact that each "catalyst" selectively absorbs those rays which polymerise formaldehyde. We have also found that 1 per cent. solutions of ferric chloride and uranyl nitrate which contain carbon dioxide give good yields of formaldehyde when exposed in quartz tubes to the light, but do not do so when a thin glass screen is interposed. The glass screen removes the very short wave-length rays which cause the formation of the formaldehyde.

It is not surprising that Moore and Webster fell into error in interpreting the function of their inorganic "catalysts," since they failed to observe any formation of formaldehyde in the absence of one of these salts, but it is curious that they did not realise the explanation of this non-production of formaldehyde, since they themselves were the first to prove that, when unprotected, the formaldehyde is polymerised to reducing sugars. It is obvious that Moore and Webster's conclusions as regards the phytosynthetic

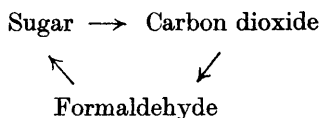
process are very materially affected. They state that the process depends on the presence of iron salts and go to some trouble to prove the presence of iron in the chloroplast. It is evident, however, that, so far from being a catalyst, the iron is really an anticatalyst, for, in the first place, it does not catalyse the formation of formaldehyde, and, in the second, it prevents the formaldehyde from polymerising to carbohydrates. Indeed, the presence of iron, if in sufficient concentration to act in the way Moore and Webster suggest, will be inimical to the growth of the plant, since the amount of formaldehyde produced will steadily increase until the plant is poisoned.

Two of the catalysts employed by Moore and Webster fall into a different category, namely, colloidal uranium hydroxide and colloidal ferric hydroxide. The explanation of the rôle played by these substances is discussed below.

Reference has been made to Moore and Webster's discovery that all substances of biochemical origin give formaldehyde when exposed in aqueous solution to ultra-violet light. This bare statement of fact is liable to mislead, because it would seem to give support to the view that these substances cannot be built up by the plant from formaldehyde. We have confirmed many of these observations, but we also find that reducing sugars are produced at the same time. Thus, whilst it is perfectly true, for instance, that a 5 per cent. aqueous solution of glycerol gives some formaldehyde on exposure to the quartz mercury lamp, a considerable amount of a reducing sugar is also produced. After only three hours' exposure to the light, sufficient sugar is produced to give a marked reduction of Benedict's solution, the total amount of sugar formed being equivalent in reducing power to 0.04 gram of glucose.

Many other substances besides those of biochemical origin give similar results, and amongst these acetone may be mentioned. An aqueous solution of acetone (1 per cent.), after some hours' exposure, gives some formaldehyde and a considerable quantity of sugar. It is well known that acetone, when photochemically decomposed, does not give formaldehyde as a direct product of decomposition, but yields formic acid, carbon dioxide, methane, etc., according to the amount of free oxygen present in the solution. It is obvious, therefore, that the formaldehyde must have been produced by photosynthesis from the carbon dioxide and water, and the question at once arises as to whether the same explanation does not apply to all carbohydrates and to chlorophyll, namely, that under the influence of light of very short wave-length they are decomposed to carbon dioxide, which is photosynthesised to formaldehyde, and this in its turn is photopolymerised to sugars.

There is no question but that under the influence of ultra-violet light an equilibrium is set up between reducing sugar, carbon dioxide, and formaldehyde, and in all probability the equilibrium may be represented by



The existence of this equilibrium is strongly supported by experimental evidence. Thus the polymerisation of formaldehyde to give a recognisable amount of sugar becomes increasingly difficult as its concentration is decreased. Again, the polymerisation will be materially enhanced if the concentration of the carbon dioxide be increased by the addition of sodium carbonate, as shown by Moore and Webster, or, better still, as we have found, of potassium bicarbonate.

It must be remembered that this equilibrium is established in ultra-violet light, and there is little doubt that the decomposition of the carbohydrate to give carbon dioxide is produced by light of very short wave-length. It is exceedingly doubtful that this decomposition would take place in the growing leaf, where the chlorophyll is only exposed to sunlight after transmission through the epidermis. We feel that Moore and Webster's statement that all substances of biochemical origin give formaldehyde on exposure to light cannot be accepted as an argument that formaldehyde is not the first stage in the photosynthesis of such substances from carbon dioxide and water.

We have already shown that carbohydrates can be photosynthesised from carbon dioxide and water in two stages, but the problem cannot be considered as solved unless it is possible to synthesise carbohydrates from carbon dioxide and water in one and the same vessel, and this we have succeeded in doing. Some difficulty was encountered at first owing to the fact that in the light of the quartz lamp the equilibrium lies very far over to the side of the carbon dioxide, and unless the concentration of this is large the amount of sugar formed is not sufficient to give a positive test. We first exposed saturated solutions of magnesium and calcium bicarbonates to the light from the quartz lamp for many hours, while carbon dioxide was being passed through them. Although strong reactions for formaldehyde were given, stronger than those obtained when a Moore and Webster "catalyst" is used, insufficient sugar was produced to cause reduction of Benedict's solution. A saturated aqueous solution of oxalic acid was then exposed for forty hours

to the light. After neutralisation and evaporation, a decided positive reaction for a reducing sugar was obtained. Under the influence of the light, the oxalic acid is decomposed to carbon dioxide, and this gives, in turn, formaldehyde and a reducing sugar. It is probable that the carbon dioxide at the moment of its formation is more active, with the result that the formaldehyde and sugar are more readily produced than from ordinary carbon dioxide in solution.

Reference may also be made to the formation of a reducing sugar when an aqueous solution of acetone is exposed to the quartz lamp. As already stated, formaldehyde is not one of the photochemical decomposition products of acetone, and therefore the formaldehyde and sugar found must have successively been synthesised from the carbon dioxide yielded by the acetone on decomposition.

If a solution of potassium bicarbonate is exposed to the light, a strong reaction is obtained for formaldehyde in a few hours, but insufficient sugar is formed to give a positive test. On the other hand, if a small amount of formaldehyde is added, sufficient reducing sugar is produced, after further exposure for a few hours, to give strong reduction of Benedict's solution.

These results clearly establish the direct synthesis of carbohydrates from carbon dioxide and water, with formaldehyde as an intermediate stage, and they also establish the fact that no catalyst is necessary. It is further evident that the equilibrium between sugar, formaldehyde, and carbon dioxide existing in the unshielded light of the lamp lies very far over to the side of carbon dioxide.

However satisfactory these results may appear to be, they do not by any means give a complete explanation of the actual process which is taking place in the plant. There is present in ordinary daylight only a very small amount of light of wave-length $\lambda=200\mu\mu$, which is necessary for the first, or formaldehyde, stage. Moreover, it is obvious that the plant juices and pigments completely absorb the ultra-violet rays, so that the photosynthesis, if dependent on these rays, could not take place. Plants grow, and during their growth synthesise carbohydrates in light transmitted through glass which completely absorbs the ultra-violet beyond $\lambda=350\mu\mu$. Finally, no formaldehyde is formed from carbon dioxide and water under the influence of light transmitted through glass. Clearly, therefore, the vital process differs markedly from the laboratory experiments already described, and the difference is that the plant uses light of longer wave-length than $350\mu\mu$, that is to say, light which is almost entirely comprised within the visible region of the spectrum. We have found that the solution of the problem lies in photocatalysis, and we have succeeded in

synthesising active or reducing sugars directly from carbon dioxide and water in two stages with the aid of suitable photocatalysts in light of longer wave-length than $350\mu\mu$, such as is used by the living plant.

In recent papers, it has been shown by one of us (Baly, *Phil. Mag.*, 1920, [vi], **40**, 1, 15) that the frequencies characteristic of any molecule in the ultra-violet are exact integral multiples of a fundamental, infra-red frequency also characteristic of that molecule, and, further, this infra-red frequency is an exact integral multiple of the frequencies characteristic of the atoms composing that molecule. Again, a definite amount of energy is required to cause a molecule to undergo a specific reaction, and this energy may be supplied to that molecule either in the form of one quantum at the ultra-violet frequency or as a whole number of quanta at one of the infra-red frequencies characteristic of the molecule or its component atoms. When the energy is absorbed at the ultra-violet frequency, the reaction is known as photochemical, and the synthesis of formaldehyde and its subsequent polymerisation by ultra-violet light are pure photochemical reactions.

It has recently been shown (Baly and Barker, this vol., p. 653) that in the photochemical reaction between hydrogen and chlorine the energy radiated during the reaction by the hydrochloric acid is partly reabsorbed by the surrounding chlorine, with the result that a great deal more chlorine and hydrogen react than corresponds with the amount of light absorbed. In this case the chlorine is activated partly by absorbing light of its own characteristic ultra-violet frequency and partly by absorbing the infra-red light radiated by the hydrochloric acid that is being formed.

It should be possible, therefore, to cause the substance *A* to undergo a photochemical reaction in light of a frequency which is not absorbed by the substance *A*. If a substance *B*, having exactly the same infra-red frequencies as *A*, be mixed with *A*, and the two be exposed to light which is absorbed by *B* and not by *A*, then the energy radiated by *B* in the infra-red will be absorbed by *A*, with the result that *A* will undergo the photochemical reaction. *B* then acts as a true photocatalyst. The criteria defining a photocatalyst are, first, that it has exactly the same infra-red frequencies as the catalyte, and, secondly, that it has a different frequency in the visible and the ultra-violet regions from the catalyte.

A typical example of photocatalysis was described by Daniels and Johnson (*J. Amer. Chem. Soc.*, 1921, **43**, 72), who showed that nitrogen pentoxide is not decomposed by blue light except in the presence of nitrogen peroxide, which absorbs blue light. The energy thus absorbed by the nitrogen peroxide is radiated at

frequencies in the infra-red which are exactly the same as those of the nitrogen pentoxide, the two compounds having the same atoms.

There is no doubt that the photosynthesis of carbohydrates in the living plant from carbon dioxide and water is a photocatalytic one, and in all probability chlorophyll or carotin is the photocatalyst. The photocatalysis consists in the absorption of light of longer wave-length than $350 \mu\mu$ by the chlorophyll or carotin and the radiation of this energy at infra-red frequencies which are reabsorbed, with the result that the carbon dioxide forms successively formaldehyde and carbohydrates. If this is the correct explanation, then it should be possible to carry out the synthesis in the laboratory, using visible light and a photocatalyst.

Since the two stages require for their experimental realisation light of different wave-lengths, they may be discussed separately. A suitable photocatalyst for the synthesis of formaldehyde from carbon dioxide and water is found in a coloured basic compound such as malachite-green, or *p*-nitrosodimethylaniline. An aqueous solution of either of these compounds saturated with carbon dioxide gives formaldehyde on exposure to light behind a thick plate-glass screen. In the absence of carbon dioxide, no formaldehyde is produced with either of the photocatalysts. A similar result is obtained with methyl-orange and with other substances.

It would seem that in the case of colloidal uranium and ferric hydroxides Moore and Webster did use true photocatalysts. There is little doubt that in each case some combination with the carbon dioxide takes place, so that the conditions for the photocatalysis are secured. This will explain why in the presence of these two substances formaldehyde is produced from carbon dioxide in visible light, as shown by Moore and Webster. It cannot be claimed that any of the photocatalysts mentioned are perfect, since they do not necessarily protect the formaldehyde entirely from the rays which polymerise it. Moore and Webster established this fact by obtaining an increased yield of formaldehyde with the colloidal uranium hydroxide solution when the vessel was surrounded by a solution of chlorophyll in alcohol. It must again be pointed out that, although the colloidal hydroxides of uranium and iron apparently act as photocatalysts in the formation of formaldehyde, they also largely protect the formaldehyde, when formed, by virtue of their power of absorbing the long-wave, ultra-violet rays. They thus prevent its polymerisation to carbohydrates, and therefore neither of them would be of any use to the growing plant.

Our results show conclusively, not only that it is possible to produce formaldehyde from carbon dioxide and water by the direct action of light of very short wave-length ($\lambda = 200 \mu\mu$), but that it

is also possible to produce the formaldehyde from carbon dioxide and water in visible light in the presence of a photocatalyst. They also entirely dispose of Moore and Webster's contention that the photocatalyst must be inorganic, since, although the metallic salts used by them are not catalysts at all, but protectors, the colloidal uranium and ferric hydroxides appear to act as photocatalysts, and for this purpose coloured organic bases act equally well.

For the second stage of the synthesis, namely, the polymerisation of formaldehyde to give active or reducing sugars, it will be necessary to employ as photocatalyst a coloured substance which forms a complex with the formaldehyde in order to secure the exact similarity between the infra-red frequencies. A suitable substance is not readily obtained, but the following experiment leaves no doubt of the photocatalysis of this polymerisation. An aqueous solution containing 17 per cent. of sodium citrate and 9 per cent. of sodium carbonate, on exposure to the quartz mercury lamp for two hours, gives formaldehyde and sufficient sugar to cause marked reduction on the addition of 1 per cent. of copper sulphate and warming. This formation of sugar does not occur if the alkaline solution is exposed to the same light behind a screen of thick plate-glass. On the other hand, Benedict's solution, which contains the same proportions of the three compounds, gives marked reduction after exposure to the light for two hours behind the plate-glass screen. This definitely establishes the photocatalysis, for the formation of the formaldehyde and its polymerisation to sugar take place within the citrate complex, which, since it contains copper, has the power of absorbing visible light, and the energy so absorbed is sufficient to cause the polymerisation to take place.

Whilst two stages in the synthesis of a reducing sugar have thus been photochemically carried out in the laboratory with and without a photocatalyst, the plant is able to synthesise carbohydrates from carbon dioxide without the formation of formaldehyde in sufficient quantities for its ready recognition in the growing leaf. It must be remembered that, if a suitable substance were obtained capable of photocatalysing both reactions in the laboratory, the separate existence of formaldehyde would not be capable of proof, since the carbon dioxide and water would give formaldehyde and carbohydrate within the same complex. We have not as yet been able to find a photocatalyst capable of acting in the dual capacity on a solution of carbonic acid, but it would seem that chlorophyll is an ideal substance for the dual rôle. Whereas every photocatalyst that we have used for the first stage does not form complexes with the formaldehyde that is produced, chlorophyll, by virtue of its structure, would seem to be capable of associating itself with carbon dioxide

and retaining the formaldehyde when formed, with the result that the process passes through the two stages to give the carbohydrate. We lay great stress on this point. The evidence in favour of the existence of free formaldehyde in growing leaves is not at all strong and thus definite proof that formaldehyde is the intermediate stage in carbohydrate synthesis is wanting. The results now brought forward certainly support the view that formaldehyde is an intermediate stage, and they also go to prove that its free existence in the leaf is not to be expected. Failure to establish its presence by the most delicate of tests can no longer be accepted as evidence against its being the first stage in the phytochemical synthesis of carbohydrates. We have not as yet carried out any experiments with chlorophyll, because we wished in the first instance to deal with the problem in the simplest possible way and to make use of photocatalysts the action of which is as simple and straightforward as possible. The use of chlorophyll at once introduces the possibility of the synthesis of optically active sugars, and we hope to investigate the behaviour of chlorophyll in the immediate future.

It is evident that the equilibrium between carbohydrate, formaldehyde, and carbon dioxide existing in the unshielded light of the mercury lamp will be entirely disturbed by a photocatalyst. In the presence of a photocatalyst which carries the reaction right through from carbon dioxide and water in visible light, the equilibrium will be shifted entirely to the carbohydrate side, since the system will be screened from those rays which decompose the carbohydrate. For this reason, as is the case in the living plant, carbohydrates will be formed when the concentration of the carbon dioxide is very small.

Conclusions.

1. An aqueous solution of carbon dioxide gives formaldehyde when exposed to light of very short wave-length ($\lambda=200 \mu\mu$).
2. An aqueous solution of formaldehyde is polymerised to reducing sugars in light of wave-length $290 \mu\mu$.
3. In the presence of paraldehyde, sodium phenoxide, and certain metallic salts which absorb light of wave-length $290 \mu\mu$, the yield of formaldehyde is materially increased. These substances do not catalyse the reaction, but protect the formaldehyde, when formed, from polymerisation.
4. The photosynthesis of formaldehyde from carbon dioxide and water can be photocatalysed by certain coloured basic substances, for example, colloidal uranium and ferric hydroxides, malachite-green, methyl-orange, etc. The photosynthesis then takes place in visible light.

5. The polymerisation of formaldehyde to give carbohydrates has also been photocatalysed.

6. When carbohydrates, glycerol, acetone, oxalic acid, etc., are exposed in aqueous solution to the light from the quartz mercury lamp, formaldehyde and reducing sugars are formed. An equilibrium is set up between sugar, formaldehyde, and carbon dioxide.

7. When exposed to the unscreened light from the mercury lamp, this equilibrium apparently lies far over to the side of the carbon dioxide.

8. By the action of the light from the mercury lamp on a concentrated solution of potassium bicarbonate considerable quantities of formaldehyde are produced, but insufficient to give a positive test for a sugar. If, however, more pure formaldehyde is added, a positive test for a reducing sugar will be obtained after further exposure for a few hours.

9. In the presence of a photocatalyst capable of catalysing both stages of the reaction, the equilibrium will be shifted entirely over to the side of the reducing sugar.

10. Chlorophyll would seem to be an ideal photocatalyst for both stages of carbohydrate synthesis from carbon dioxide and water. The formation of carbohydrates in the growing leaf from very small concentrations of carbon dioxide without the free existence of formaldehyde as an intermediate product is thus explained.

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