ON THE BEHAVIOR OF NICKEL CARBONATE IN RELATION TO PHOTOSYNTHESIS

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Professor E. C. C. Baly (1927, 1928, 1929) claims to have synthesized carbohydrates by the action of visible light on an aqueous suspension of finely divided nickel carbonate saturated with carbon dioxide. He describes the production of weighable amounts of carbohydrate, of the order of 1 gm., by the action of 50 gm. of nickel carbonate.

To produce 1 gm. of glucose from carbon dioxide and water, approximately 0.95 gm. carbon dioxide is necessary. Under standard conditions this amount of carbon dioxide has a volume of 480 cc. One ten thousandth of this amount (48 c. mm.) would be easily measurable in a Barcroft-Warburg manometer, of the type commonly used.

It should therefore be possible to determine whether the appearance of Baly's carbohydrate is accompanied by the disappearance of a corresponding amount of carbon dioxide, and the production of a corresponding amount of oxygen. In any proof that artificial photosynthesis takes place, this should be an important step. It is omitted by Baly and his collaborators.

In this paper the writer describes experiments designed to demonstrate if possible the disappearance of carbon dioxide and the appearance of oxygen, when an aqueous suspension of nickel carbonate is exposed to visible light.

I

Preparation of the Nickel Carbonate

Nickel carbonate was prepared according to Baly's rather meager directions, by the electrolysis of a saturated solution of carbon dioxide in redistilled water with

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nickel electrodes. Baly states that with three electrodes 8" × 5" × 3/8" he used 220 volts, and "sufficient resistance intercalated to reduce the current to about 2 amperes." He does not state the distance between his electrodes. The writer tried various distances, but was unable to make a similar system to conduct more than 0.5 amperes at 220 volts without any resistance. Using tap water, or commercial distilled water, the system conducted readily. It was concluded that some additional substance must have been present in Baly's system, to give such a high conductivity. If the current density is too low, no nickel carbonate is formed. Traces of various electrolytes were added to redistilled water to make it conduct enough current to produce a good yield of nickel carbonate. Hydrochloric acid was found to be most satisfactory. 0.5 cc. of "c.p." hydrochloric acid diluted 1 to 10 was added to 3 liters of electrolyte.

The precipitated carbonate was centrifuged off, dried to 100°C., heated to 135°-140°C. for 30 minutes, powdered in an agate mortar, passed through a 200-mesh phosphor-bronze sieve, spread in a thin layer in a crystallizing dish covered to protect from dust, and just prior to use illuminated for 12 to 18 hours by a 100 watt lamp at about 7 inches distance.

The substance prepared in this way is surely a basic carbonate of nickel. Heating to 135°-140°C. turns it a darker green, and it loses CO₂ which it can readily take on again. Heating to higher temperatures blackens it, and all the carbonate is converted to oxide. To obtain some idea of the composition of the preparation, samples which had been dried at 100°C. and not heated to 135°C. were weighed into a crucible, ashed, and the loss in weight determined. Assuming the residue to be nickel oxide, the carbonate preparation was found to contain 40 per cent nickel. To determine the amount of CO₂ present in the carbonate, weighed samples were treated with normal sulfuric acid, and the evolved CO₂ measured manometrically. The preparation was found to contain 8.75 per cent CO₂. Gmelin-Kraut (Handbuch der anorgischen Chemie, Heidelberg, 1909, 5, Part 1, 108-109, 7th edition) states that basic nickel carbonate is of variable composition, and gives as example 3 NiO, CO₂, 6H₂O. This gives nickel 46.8 per cent, and CO₂ 11.7 per cent, figures not differing greatly from those of the writer.

II

Manometric Experiments

Samples of recently irradiated powder were weighed into the bulbs B of vessels of the type shown in Fig. 1. The main chamber C was given 3 cc. of redistilled

1 The electrodes were furnished through the courtesy of the International Nickel Company.
water saturated either with 100 per cent CO₂ or with a mixture of 5 per cent CO₂ in air. The vessels were connected with their manometers, filled with the gas used to saturate their contents, and shaken in a thermostat at 20°C. until equilibrium was reached. The contents of the bulb was then washed into the main chamber, without opening the system.

The behavior was followed in continuous light or dark, or in intermittent light, by frequent readings of the manometers. All preparations absorbed carbon dioxide rapidly, absorption being most rapid with 100 per cent CO₂ in air. After mixing, the rate of CO₂ absorption rose rapidly to a maximum, and then fell off slowly, continuing at a decreasing rate for 4 or 5 hours. The course of absorption of a typical sample in 100 per cent CO₂ is shown in Fig. 2, total amount of CO₂ absorbed being plotted against time.

The curve shows the absorption of CO₂ by 8.5 mg. of nickel carbonate over a period of 5 hours and 10 minutes. At the end of this time, CO₂ was still being taken up perceptibly, though slowly. In all, 1825 c. mm. of CO₂ were absorbed by 8.5 mg. of carbonate in the period of observation.

The process is reversible at any point. Air may be substituted for 100 per cent CO₂, and the absorbed gas is then evolved. Much of the
CO₂ goes to forming a soluble nickel compound, possibly a bicarbonate, which can be precipitated if the CO₂ is pumped off.

A variety of combinations of CO₂ concentration, light intensity, and nickel carbonate samples were tried, but no effect of illumination could be observed. Illumination for short and long periods, of intensities from 10,000 to 100,000 Lux were tried, without any effect on the rate of CO₂ absorption.

Baly states that his preparations became inactive through the accumulation of oxygen. Some experiments were therefore tried with
small sticks of white phosphorous in the central well \( D \) of the manometer vessel, to absorb any possible oxygen, but no difference in behavior could be detected.

III

Gas Analysis Experiments

It was thought possible that a small photosynthesis might be concealed in the rapid absorption of \( \text{CO}_2 \) which was continuous in light or dark. Several analyses were made of the gas taken from above illuminated samples of nickel carbonate in water, in an attempt to demonstrate the production of oxygen during illumination.

Fig. 3. Type of vessel used for gas-analysis experiments. The long stop-cocks are used to avoid having grease come in contact with the material under investigation.

Vessels of the type shown in Fig. 3, having a total volume of about 12 cc., were filled with 3 or 5 cc. of redistilled water saturated with the desired gas mixture. Just before closing the vessel, 50 to 500 mg. of nickel carbonate were added. The vessel was then shaken in either light or dark in a water thermostat for 2 to 5 hours. Analyses were made with an apparatus of the Haldane type on which one scale division was equal to 10 c. mm. No oxygen was ever detected as a result of illumination.

IV

Direct Test for Carbohydrates

The experiments described above were all carried out in closed vessels, whereas Baly’s experiments were made in a continuous stream of carbon dioxide. A system similar to Baly’s was devised as follows:
A glass cuvette of about 50 cc. capacity and 9 mm. distance between inside walls was filled with double-distilled water, and a stream of 100 per cent CO₂ was bubbled rapidly through. About 200 mg. of a fresh sample of nickel carbonate was added. The cuvette was illuminated by a 100-watt lamp 25 cm. away for five hours. The nickel carbonate was then centrifuged off, and the supernatant fluid concentrated in vacuo. The carbonate which precipitated out during concentration was separated off at intervals. The fluid was concentrated to a fraction of a cubic centimeter, and treated with sulfuric acid. There was no visible charring.

CONCLUSION

The writer was unable to prepare a sample of nickel carbonate which would give any indication of photosynthetic activity. If Professor Baly's preparations are really active, I believe there is some detail in his procedure which he has failed to mention.

LITERATURE CITED