abgesaugt und wiederholte Male aus einem Gemisch Benzol-Chloroform (2:1) unter Zusatz von A-Kohle umkristallisiert wurde. Ausbeute: 2.5 g (69% d. Theorie). Schmp. corr. 233.4—234.0 °C.

C_{14}H_{9}NO_4 (255,22)

Ber. N 5,49,

Gef. N 5,32 ; 5,33.

1.4-Dihydroxy-anthracinon-2-carbonsäure-methylester

Er wurde durch Veresterung der 1.4-Dihydroxyanthracinon-2-carbonsäure dargestellt. Rote Nadeln; Schmp. 182—184 °C.

3-Formyl-5-methyl-salicylsäure-methylester

9 g 3-Formyl-5-methyl-salicylsäure wurden in 300 ml 99-proz. Athanol gelöst und unter starkem Rühren mit 9,3 g Silbernitrat in 25 ml Wasser versetzt. Nach zehnminütigem Rühren wurde das weiße Silbersalz abgesaugt, mit Äthylalkohol und schließlich mit Äther gewaschen und im Vakuum getrocknet.


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Porphine-like substances: III. Synthesis by electrical discharge

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Electrical discharge between an electrode connected to a Tesla coil and the surface of an aqueous suspension of a mixture of pyrrole and benzaldehyde produces porphine-like substances. Among others the compound α,β,γ,δ-tetraphenylporphine (TPP) has been identified by 1. Separation of the compound by the thin layer chromatographic technique using silica gel and two percent xylene in benzene as adsorbent and developing mixture respectively. 2. Visible spectra of the base and of the zinc-chelate of the compound compared with the spectra of the reference TPP. Storage of the irradiated mixture either in benzene or as aqueous suspension increases the total yield. This increase is a function of time of storage. The results obtained in this set of experiments are similar to previously reported results in which Co-60 gamma, ultraviolet, and visible radiations were used as sources of energy. These results imply that the formation of porphine-like substances is biogenically possible under primitive earth conditions.

The appearance of the first living cell on the earth was preceded by chemical evolution i.e., evolution on the molecular level. It has been agreed by scientists that the early Earth's atmosphere, under constant action of ultraviolet, visible and nuclear radiations and electrical discharges, was constantly changing due to the formation of more complicated molecules 1-4. This atmosphere, reductive in its character, is believed to have consisted of methane, ammonia, water and hydrogen. At some time it started to change into an oxidative one, due to the appearance of molecular oxygen which was being formed by photolysis and radiosynthesis of water vapor. Through the action of ultraviolet radiation and electrical discharges on the molecular oxygen ozone was formed, which shielded the Earth's surface from the short ultraviolet radiation. At the same time, the photolysis and radiosynthesis of water produced large amounts of molecular oxygen.


quantities of hydrogen peroxide, which in contact with organic compounds would destroy them. Therefore, an evolutionary pressure was exerted on the system to:

1. utilize visible radiation instead of ultraviolet for further chemical reactions and
2. destroy the accumulated hydrogen peroxide. It has been shown by Calvin that porphines, or better porphines with a protein moiety, known as catalase, are very effective catalysts for the destruction of hydrogen peroxide into \( H_2O \) and \( O_2 \). At the same time, porphines, being highly colored substances, are capable of absorbing visible light and utilizing this energy for certain chemical reactions. It is known that with the aid of porphyrins and especially their metal chelates, chemical transformations such as hydrogen transfer or oxidations can occur.

Thus the abiogenic formation of porphines and porphine-like substances is, for exobiologists, of utmost importance.

It has been shown in our previous papers that porphine-like substances, specifically \( \alpha,\beta,\gamma,\delta \)-tetraphenylporphine, can be formed abiogenically. These papers also present the effects of Co-60 gamma-radiation and ultraviolet and visible radiations on the rate of formation of TPP. \( \alpha,\beta,\gamma,\delta \)-tetraphenylporphine has been selected as a model for porphine type of structure because it is easy to isolate and identify. This paper presents another observation having direct bearing on the formation of the organic milieu, namely the synthesis of porphins from simple precursors and the effect of electrical discharges in reductive and oxidative atmospheres on the yields of porphines.

**Experimental**

In a typical experiment, a mixture of two milliliters of freshly distilled pyrrole, four milliliters of benzaldehyde and four milliliters of double distilled water was placed in an irradiation vessel (approximately 30 cc. in volume). This mixture, except for the solvent is identical with the mixture used in experiments of Ball, Dorough and Calvin. When using a reductive atmosphere, the vessel was connected to an apparatus which allowed methane, ammonia and hydrogen to come in contact with the mixture during irradiation. The partial pressures of the gases in the vessel before irradiation were 8.7 cm of hydrogen, 8.4 cm of ammonia and 8.7 cm of methane with the remaining pressure due to water and organic vapors. When using an oxidative atmosphere, a water condenser was connected to the side-arm of the vessel. Ordinary air entered the vessel through the condenser. A tesla-coil (Electro Technic Products, Chicago, Illinois) was used to produce the electrical discharge. Samples were irradiated for two and four hour periods in semi-darkness.

After each run, the temperature and \( pH \) of the mixture were recorded. The temperature of the mixture varied from 40—60 °C, while the \( pH \) varied between 4 and 6. The products of the reaction were then poured into a separatory funnel to which were added 25 milliliters of water and the benzene washings from the reaction vessel. After separation from the aqueous-layer was complete, the benzene-layer was placed into a beaker charged with 10 grams of anhydrous sodium sulfate to remove traces of water. The solution was filtered through a paper filter into a 50 milliliter volumetric flask. The separation of tetraphenylporphine was accomplished by a modified procedure developed in our laboratory. With the use of a syringe, 25 micro-liter quantities of the product were spotted on thin-layer chromatographic plates having a 200 micron thick layer of dehydrated silica-gel. The plates were placed for two hours into a tank containing 200 milliliters of a solution of 2% xylene in benzene. After the plates were taken out of the tank and dried the porphine bands were scraped into long-stem funnels blocked with cotton plugs. The porphine was eluted with benzene and the volume of porphine solution made up to 3 milliliters for all samples.

The porphine which was isolated was identified as tetraphenylporphine by visible spectra of the free base and its zinc complexes. The spectrum of \( \alpha,\beta,\gamma,\delta \)-tetraphenylporphine was recorded on a Bausch & Lomb Spectronic 505, and the total yield per 50 milliliter sample was calculated from molar-extinction coefficient of \( 4.78 \times 10^5 \) at 418 millimicrons.

**Results and Discussion**

The results obtained are summarized in Fig. 1. In this Figure the total yields in mg per sample were plotted versus the time of storage in days. Firstly, two hour runs in a reductive atmosphere, are compared with runs which occurred spontaneously in...
the presence of molecular oxygen, i.e. without the use of electrical discharges. The increase in the yield of TPP with time indicates that a process of autocatalysis takes place. This process, postulated by Calvin$^5$, now can be supported by experimental evidence. The changing value of the slope can be explained by considering the environmental conditions of the experiment. It can be argued that in the initial stages of the reaction, the rate of formation by autocatalysis is slow, as represented by the small slope. The sample in benzene was stored in contact with air containing molecular oxygen. As the solution became saturated with air, due to daily mixing, the slope increased. This in turn would indicate that molecular oxygen is necessary for the reaction to occur. Adler, Longo and Shergalis$^9$ in their study also came to the conclusion that oxygen participates in the reaction leading to the formation of porphines.

Similar results were obtained from runs in an oxidative atmosphere, as compared with runs which occurred spontaneously. It can be seen that the slope of the curve, which represents the rate of formation of TPP upon standing has a constant value, because the solutions were equilibrated with air, and therefore the molecular oxygen is available for the synthesis. The results of comparison of runs exposed two and four hours toward electrical discharges indicate that there is no increase in the yield of TPP upon standing as observed in previous cases. In this case, it is suggested that the synthesis of TPP proceeds through the formation of a labile intermediate which can be easily destroyed by reaction products of the electrical discharge. Apparently the four hour exposure of the sample to electrical discharge destroys most of the intermediate such as $\alpha,\beta,\gamma,\delta$-tetraphenylchlorin, but this requires confirmation.

Therefore, we can speculate about the sequence of events leading to the formation of porphyrins and chlorophylls as follows: Due to the evolutionary pressure, as outlined above, the porphines appeared in the organic milieu by spontaneous processes. In order to survive the high flux of energy reaching the surface of the earth from solar radiation or electrical discharges they had to be transformed into more stable compounds, perhaps metal chelates, or buried in the depths of oceans. Thus, their function as catalysts for the destruction of hydrogen peroxide and as catalysts for the more complicated photochemical evolutionary processes would be preserved. Porphines destroyed by the action of energies were replenished by autocatalysis, which operated on the system, thus preserving the concentration needed for further chemical evolution.

It must be pointed out that we do not suggest that the $\alpha,\beta,\gamma,\delta$-tetraphenylporphine, was the compound involved in the destruction of hydrogen peroxide and in the problem of energy supply for more complicated organic synthesis during chemical evolution. We merely regard it as a model compound.

The above results have shown that porphine-like substances can be formed abiotically in the presence of reductive and oxidative atmosphere with 2 and 4 hours exposure to electrical discharges. The synthesis is believed to proceed through the formation of an intermediate, which then autocatalytically, in the presence of molecular oxygen, changes into the final product, i.e. tetraphenylporphine.

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