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PORPHINES-LIKE SUBSTANCES: III.
SYNTHESIS BY ELECTRICAL DISCHARGE

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23374 ABSTRACT

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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 $\alpha,\beta,\gamma,\delta$ -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 zinc-chelate of the compound compared with the chelate of the reference TPP. The yields of the compound in the presence of molecular oxygen, are increased over the yields obtained in runs performed under primitive atmosphere i.e. methane, ammonia and molecular hydrogen. 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 abiogenically possible under primitive earth conditions. This work was supported in part by Grant NsG-226-62 from the National Aeronautics and Space Administration.

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Introduction

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, consisting of methane, ammonia, water and hydrogen under constant action of ultraviolet, visible and nuclear radiations and electrical discharges was constantly changing due to the formation of more complicated molecules.^(1,2,3,4) This atmosphere, reductive in its character, at some time started to change into an oxidative one, due to the appearance of molecular oxygen which was being formed by photolysis and radiolysis 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 radiolysis of water produced large 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 the visible radiation instead of ultraviolet for further chemical reactions and
 - 2) destroy the accumulated hydrogen peroxide.
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It has been shown by Calvin (5,6) that porphines or better porphines with a protein moiety, known as catalase, are very effective catalysts for the destruction of hydrogen peroxide. At the same time porphines begin highly colored substance 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 could occur.

Thus the abiogenic formation of porphines and porphine-like substances is for exobiologists or those interested in the formation of living systems, of outmost importance.

It has been shown in our previous papers (7,8,9) that porphine-like substances, specifically $\alpha, \beta, \gamma, \delta$ -tetraphenylporphines, 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. The $\alpha, \beta, \gamma, \delta$ -tetraphenylporphines, has been selected as a model for this type of compound structure.

This paper presents another observation having direct bearing on the formation of the organic millieu, namely the synthesis of porphines from simple precursors and the effect of electrical discharges and reductive and oxidative atmospheres on the yields.

Experimental

In a typical experiment, a mixture of two milliliters of freshly distilled pyrrol, four milliliters of benzaldehyde and four milliliters of double distilled water was placed in an irradiation vessel (approximately 30 cc. in volume). 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 gasses 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 was 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 was added 25 milliliters of water and the benzene washings from the reaction vessel. The funnel was shaken and then left to stand until a separation of the benzene-layer

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. With the use of a syringe, 25 microliter 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 we isolated was identified as tetraphenylporphine by visible spectra of the free base and its zinc complexes.

The spectra of $\alpha, \beta, \gamma, \delta$ -tetraphenylporphine were recorded on a Bausch & Lomb Spectronic 505, and the total yield per 50 milliliter sample was calculated from molar-extinction coefficient of 4.78×10^5 at 418 millimicrons.

Results and Discussion

Fig.1 represents the results obtained from runs in a reductive atmosphere, as compared with runs which occurred spontaneously, in presence of molecular oxygen. i.e. without

the use of electrical discharges. It is a plot of total yield in mg per sample versus the time of storage in days. The increase in the yield of TPP with time indicates that a process of autocatalysis takes place. This process, postulated by Calvin, now can be supported by experimental evidence. The continuous change in the slope can be explained by considering the environmental conditions of the experiment. It can be argued that in the beginning the rate of formation by autocatalysis is slow, as represented by the low slope. The sample in benzene was stored in contact with air containing molecular oxygen. As the solution became saturated with air the slope increased. This in turn indicates that molecular oxygen is necessary for the reaction to occur.

Fig. 2 represents similar results obtained from runs in an oxidative atmosphere, as compared with runs which occurred spontaneously. In this case it is also a plot of total yield in mg per sample versus time of storage of the sample in benzene. It can be seen that the slope of the curve, which represents the rate of formation of TPP upon standing by auto-catalysis has a constant value, because the solutions were equilibrated with the air, and therefore the molecular oxygen is available for the synthesis.

Fig. 3 represents superimposed Figures 1 and 2 and underlines the differences in the initial slopes, as discussed previously. It can be seen that both lines finally reach a point where the slopes are the same.

Fig. 4 represents the same plot of yield versus the time of storage for a sample, which has been exposed to four hours of electrical discharge, as compared to two hours for the previous three slides. The results indicate that there is no increase in the yield of TPP upon standing as observed in previous cases. The tentative explanation of the results is as follows. 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 as $\alpha, \beta, \gamma, \delta$ -tetraphenylchlorin, but this requires confirmation.

In conclusion, we have shown that porphine-like substances can be formed abiogenically in presence of oxygen and not too prolonged exposure toward electrical discharges. The synthesis proceeds through the formation of an intermediate, which then autocatalytically changes into the final product.

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