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PHOTOCHEMISTRY OF PORPHYRINS (thesis)

By
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November 1953

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Table of Contents

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ABSTRACT

With a view to the possible bearing on the understanding of photosynthesis, a study has been made of the photochemical hydrogenation of a synthetic porphyrin, zinc tetraphenylporphin. A number of substances, including benzoin, ascorbic acid, dihydroxyacetone, hydrazobenzene, and hexyl mercaptan, show ability to hydrogenate the porphyrin in the presence of light. The principal reduction product has been identified as tetrahydroporphin, and its spectrum has been established. Also found under special conditions is a compound believed to be zinc hexahydrotetraphenylporphin, which is oxidized by oxygen in the dark to tetrahydroporphin.

The kinetics have been investigated of the fastest of these reductions, that by benzoin. The reaction rate was found to be proportional to a power higher than first of the light intensity; in fact, it is directly proportional to the amount of light absorbed by benzoin, and augmented by light absorbed by the porphyrin. The reaction, however, will not go if only light absorbed by the porphyrin is used. This light-intensity dependence can be satisfactorily explained by postulating that reaction may occur when a molecule of benzoin in a triplet excited state collides with a molecule of porphyrin, in its ground state or in its triplet excited state. The quantum yield at high light intensities, based on light absorbed by benzoin, is about 0.06.

The photochemical oxidation of zinc tetrahydrotetraphenylporphin to zinc tetraphenylporphin by phenanthraquinone has also been studied. The reaction rate is proportional only to light absorbed by the tetrahydroporphin, and the quantum yield is 4×10^{-4}. It is proposed that reaction occurs when triplet excited molecules of tetrahydroporphin collide with ground state phenanthraquinone.

Zinc tetraphenylporphin is slowly destroyed by oxygen in the light. A number of substances, including benzoin, exert a marked catalytic effect. The rate of destruction of zinc tetraphenylporphin by oxygen in the presence of benzoin has

been found proportional to the amount of light absorbed by the benzoin, and a me-
chanism has been proposed involving transfer of oxygen from benzoin to porphyrin.

Certain correlations have been made between the spectra and the structures of
the porphyrins. The nature of the metal in the center of the porphyrin ring has
been correlated with the fluorescence, magnetic susceptibility, and stability of
the metal porphyrin complex. On the basis of an examination of the spectral and
chemical evidence, a revised structure for bacteriochlorophyll, a naturally-occur-
ring tetrahydroporphyrin, has been proposed.

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INTRODUCTION

Of all biochemical reactions, the most fundamental is photosynthesis, where-by green plants convert solar radiation into chemical energy. It has long been known that the chlorophylls, present in all green plants, are the agents primarily respon-sible for absorption of light, but the means by which light energy is used to make sugar out of water and carbon dioxide has, until recently, been entirely unknown. However, the fact that chlorophyll is partially dehydrogenated porphyrin has quite naturally led to the hypothesis that the photo-excited state of chlorophyll either hydrogenates or dehydrogenates a suitable substrate such as DPN or DPN-H_2, with a net increase in the free energy of the system. The chlorophyll would, in this hypothesis, be regenerated by exothermic hydrogenation or dehydrogenation. The present work is part of an attempt to study, on a system much simpler than chloro-phyll, those photochemical oxidations and reductions of which porphyrins are ca-pable, in the hope of testing this hypothesis.

The porphyrin used for these experiments is the one most easily obtained, the zinc complex of a, b, c, d-tetraphenylporphin.[1,4] At this laboratory, the photochemi-cal oxidation of the dihydrogen derivative of the above porphin, zinc tetraphenychlorin, has been studied by Ball, Dorough, and Huennekens.[5,20] They found that the chlorin (dihydroporphin), irradiated in benzene solution containing a quinone, was converted smoothly and quantitatively into porphin. They found that the rate of the reaction was directly proportional to the amount of light absorbed by the chlorin, and inde-pendent of the quinone concentration, down to very low values. The rate was, how-ever, found to depend on the oxidation potential of the quinone, and orthoquinones were found to be more rapid oxidizers than paraquinones of the same oxidation potential. A small negative temperature coefficient of the reaction rate constant was found. The copper chlorin complex, which is paramagnetic, was found to react at less than one hundredth the speed of the zinc complex. The quantum yield was about 0.002. These facts led Dorough and Huennekens to postulate that the chlorin, on absorbing light, passed over into a long-lived triplet state, in which state it reacted with quinone.
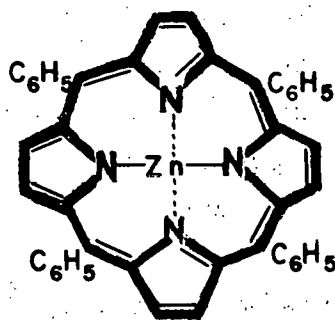
Zinc Tetraphenylporphin
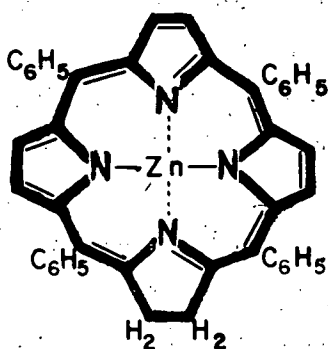
Zinc Tetraphenylchlorin

Fig. 1
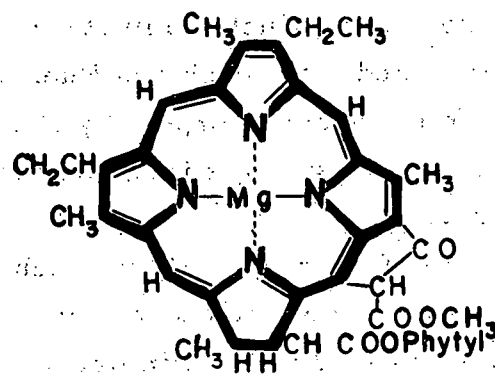
Chlorophyll a
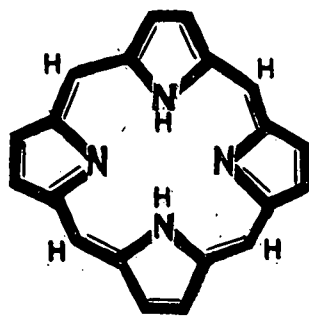
Porphin

Fig. 2

The primary work of this thesis is an attempt to reverse this reaction, that is, to reduce zinc tetraphenylporphin photochemically, and to find, if possible, the mechanism.   Chemical reductions of zinc porphin are known: Dorough, in his Ph. D. thesis, reported finding various products on reduction with sodium and alcohol, [7,2] and has recently reported the isolation of two tetrahydroporphins from catalytic hydrogenation of free base tetraphenyl-chlorin. [12]   The yield of isolable product is minute in both these cases, since the reaction cannot be controlled.   Dorough and Huennekens also report photochemical reductions of zinc tetraphenylporphin by phenylhydrazine and hydrazo-benzene,   requiring extremely high light intensities, and producing a compound having an absorption band at 600 mμ. [7,19]

Owing to the importance of ascorbic acid in biochemical systems, and to reports by Krasnovskii and his associates that photoreductions of chlorophylls and magnesium pheophytin by ascorbic acid in pyridine solution have been obtained, [23] we decided to try to reduce zinc porphin first of all with ascorbic acid, in pyridine solution.

PREPARATION OF ZINC TETRAPHENYLPORPHIN

Synthesis

The zinc complex of tetraphenylporphin is prepared directly, according to the procedure originally described by Rothemund,[39,40] with a few modifications. The best results have been obtained by heating 5 cc. of pyrrole, 10 cc. of benzaldehyde, 15 cc. of pyridine, and 5 g. of zinc acetate together at 180°C in a sealed tube for four days. The pyridine and the pyrrole are first dried over potassium hydroxide or barium oxide and distilled. The benzaldehyde is washed with soda to remove benzoic acid, and distilled. These are stored under nitrogen to prevent discoloration or oxidation. Zinc acetate dihydrate, which is commercially available, is rendered anhydrous by heating in a test tube on a steam bath under the reduced pressure of a water aspirator, which draws a slow current of dried air through the finely ground crystals.

The reagents listed above are put into a thick-walled pyrex tube of about 50 cc. capacity, sealed at one end. The contents are flushed with nitrogen, and the other end of the tube is drawn out and sealed. The pyrex tube is then placed inside a steel pipe with a screw cap on one end, to guard in case of explosion. The pipe is placed in an electric furnace, the current through which is controlled by a variable transformer.

When the reaction is deemed over, the tube is cooled and opened. The tar is filtered, with suction, through a sintered glass crucible or Buchner funnel, leaving behind crystals of zinc tetraphenylporphin, which may be washed with a little acetone or acetone-and-ether mixture. Included tar may be largely removed by mixing the crystals thus obtained with acetone in an evaporating dish, allowing evaporation of the acetone, and separating the porphin crystals at the bottom of the dish from the tar on the walls. Porphin prepared this way contains very little tarry material, but does contain a little chlorin, and traces of other colored materials. Such porphin was used for the earlier qualitative experiments on reduction. The best yield, obtained using the conditions cited at the beginning of this section, was 17 percent based on pyrrole. If less pyridine is used, or if the mixture is heated longer, the tar is inconveniently thick; on the other hand, if for any reason the tar is thin, a second crop of porphin may be obtained by evaporating the filtrate.

Attempts have been made to prepare directly other metal porphin complexes by using other metal acetates in place of zinc. The only run at all successful employed copper acetate, and gave a yield of about three percent copper porphin. Runs using nickel acetate, magnesium acetate, and basic ferric acetate were all unsuccessful. The conditions used in these runs were the same as those employed for zinc.

Chromatography

Porphin as prepared above is satisfactory for qualitative exploratory experiments; in fact, since it contains a little chlorin, it is better than pure porphin, for the chlorin may undergo a reduction which the porphin does not. But for quantitative work the porphin must be purified, and the best way to do this is by chromatography.

Previously this has been done by the method used by Ball, Dorough and Huennekens: talc is the adsorbent, trichloroethylene the solvent. This method, although generally satisfactory, has three minor disadvantages: wet talc is grey, making it more difficult to see bands on the column; trouble is sometimes encountered in eluting the porphin from the talc; in the presence of oxygen, trichloroethylene photolyzes to give acid chlorides, which hydrolyze to give hydrogen chloride, which in turn may decompose the zinc complex. In this last matter, it may be noted that Dorough reports that the free base, tetraphenylporphin, appears as a green band when chromatographed with trichloroethylene, whereas we have noticed it appears as a red band when chromatographed with benzene. Red is the color of the free base; green is the color of the hydrochloride.

Scanning the field, starch and calcium carbonate were found too weak, but magnesia and alumina, although stronger adsorbents than talc, permitted good separation of bands. A procedure has been developed which is reasonably fast, and which permits preparation in one operation of zinc porphyrin whose spectrum agrees quantitatively with that reported by Dorough.

The column, which is about 20 cm. long and two cm. in diameter, is packed with a mixture of 2/3 magnesia and 1/3 hyflo super-cel, poured in as a slurry in benzene. The benzene should first be dried over calcium oxide. The porphin is dissolved in a small quantity of benzene, and put onto the column, gentle suction being required. From five to ten mg. of porphin may be handled conveniently on a column of this size. Development may be done with benzene alone, or about one drop of pyridine may be added to five cc. of benzene for faster development. The pyridine concentration may be increased as development proceeds, but excess pyridine should be avoided at first, because of its considerable solvent power on all porphyrins. The column is extruded, and water is added to the part containing zinc porphin. The benzene solution of porphin, which is released on slaking the magnesia, may be filtered into a weighing bottle and evaporated.

This procedure is satisfactory for all porphyrins that are stable in the presence of water. On the column, the porphin forms the lowest band, chlorin next;

the trace impurities lie near the top. An oxygen-containing solvent, like dioxane, appears to have greater eluting power for the impurities than for the porphin, and so should be avoided in developing.

It should be remarked that if pyridine is used in the development, on evaporation of the solvent, zinc porphin crystallizes as the monopyridinate.[11] For example, in one such experiment, evaporation of the solution eluted from the column in the air at about 40° C yielded 12.4 mg. of pyridinate. It required two hour-long periods of drying in a vacuum oven at 115° to drive off the pyridine, leaving 11.2 mg. of zinc porphin. This corresponds quite closely to a one-to-one ratio of porphin to pyridine.

PHOTOCHEMICAL EXPERIMENTS ON PORPHYRINS

Photochemical Reductions of Zinc Tetraphenylporphin

Before discussing the results of the photochemical reduction experiments, let us look at the spectra of zinc porphin in various solvents, for it is by observing changes in the spectrum that the progress of the reactions may be followed.

The spectrum of zinc tetraphenylporphin is composed of a series of bands in the visible, centering about the green; a very intense band in the violet, known as the Soret band; and two or three distinguishable bands in the ultraviolet, of intensity like that of the band in the green. It is with the visible-band series of long wave length, the "green" band, that we shall be concerned. The positions and extinction coefficients of the several maxima of this band region of zinc tetraphenylporphin change with the solvent. Consider the series:

aliphatic hydrocarbons

benzene

oxygen-containing solvents: dioxane, alcohols, ketones

basic solvents: pyridine, piperidine, pyrrole.

As we proceed down the series, all peaks shift to the red; in particular, the highest peak shifts from 545 mμ in hydrocarbons to 550 in benzene to 555 in alcohol to 563 in pyridine. Its extinction coefficient decreases slightly down through the series. The extinction coefficient of the peak of longest wave length increases considerably as we go down the series.[*]

---

[*] Our extinction coefficients for porphin in benzene solution agree with Dorough's within our experimental error; his values are probably better, so they are recorded in Table I. The exact values in pyridine solution perhaps depend on the pyridine concentration; our own are recorded here. Dorough's may be found in bibliography reference 10. The extinction coefficients in alcohol solution are our own.

TABLE 1

Extinction Coefficients of Zinc Porphin in Three Solvents

Benzene		Ethanol		Pyridine	
λ, band max.	$\epsilon \times 10^{-3}$	λ, band max.	$\epsilon \times 10^{-3}$	λ, band max.	$\epsilon \times 10^{-3}$
"Green"				Band	
587 mμ	3.7	594 mμ	7.5	602 mμ	10.2
549	22.2	555	21.4	563	19.9
512	3.1	518	3.2	525	3.5
482	1.5	489	1.3	493	1.5
Soret				Band	
422	590.0	420	815.0	429	660.0
402	40.0	399	54.0	407	42.0
---		383	9.3	389	7.2
Ultraviolet				Band	
348	10.3	352	11.5	355	10.9
316	14.0	314	18.4	320	18.0

SPECTRA OF ZINC TETRAPHENYLPORPHIN IN THREE SOLVENTS
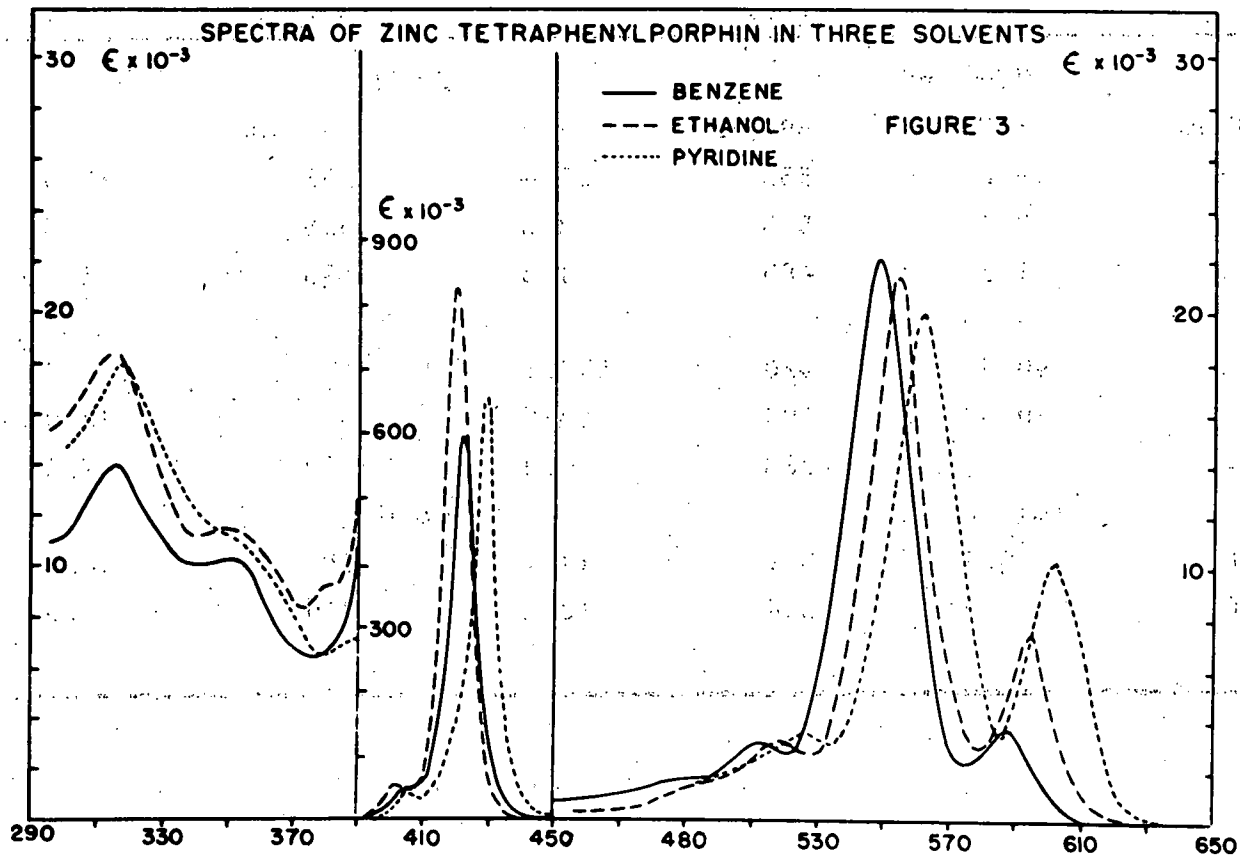
BENZENE
ETHANOL   FIGURE 3
PYRIDINE

Fig. 3
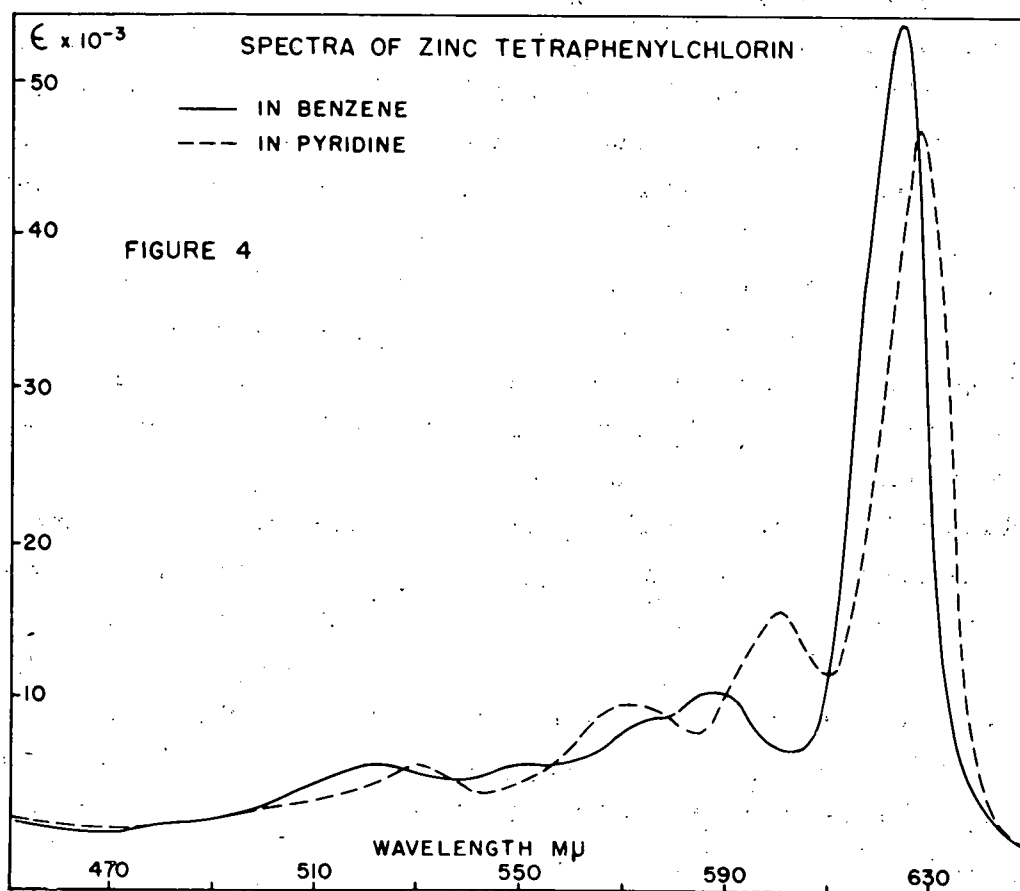
Fig. 4

Zinc tetraphenylchlorin is characterized by a strong band in the red at 618 mμ in benzene, and 623 mμ in pyridine.[*]

The progress of many of the reactions to be listed was followed visually, using a Bausch and Lomb table spectroscope, but for permanent records, a Beckman spectrophotometer and (later) a Cary recording spectrophotometer were used. The reactions were run in small pyrex tubes of square cross section, of 0.96 cm. inside width, and of volume of about 4.5 cc., which fit in cell holders in the spectrophotometers. It was necessary to exclude oxygen from the reaction; this was done, in the earlier experiments, by bubbling tank nitrogen which had been washed by either Fieser's solution or chromous chloride through the solution in the tubes, then capping the tubes with a head that permits evacuation, as an extra precaution. A better arrangement, used for quantitative work, is described later. Illumination was usually by sunlight, although occasionally artificial sources were used.

Attempts to reduce zinc porphin in pyridine by ascorbic acid photochemically were not very successful, although when pyridien was wet, reduction was detected by a change in spectrum and change of the color of the tube from purple to green. It was observed that if air was present, the porphin in pyridine solution was eventually completely decomposed by sunlight.

Ascorbic acid owes its reducing power to the presence of an enediol group. Another compound with an enediol group, or perhaps rather the tautomeric alpha-hydroxy-ketone, is benzoin. Attempts to reduce with this reagent were quite successful.

Reductions with benzoin were carried out both in pyridine and in benzene solutions, usually in sunlight. With pyridine as a solvent, illumination produced at first a marked rise in the 623-mμ band, characteristic of zinc tetraphenylchlorin, with a corresponding fall in the 563-mμ band of porphin. Further illumination gave rise to a band at 606 mμ, accompanied by eventual decrease in the chlorin band, and continued decrease in the porphin band. Eventually, all porphin and chlorin were gone, leaving only a compound characterized by an intense absorption band at 606 mμ. On prolonged exposure to sunlight, this band, too, faded, leaving nothing identifiable.

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[*]   The spectrum of zinc chlorin in benzene is taken from Dorough's thesis; the spectrum in pyridine is from bibliography reference no. 11.
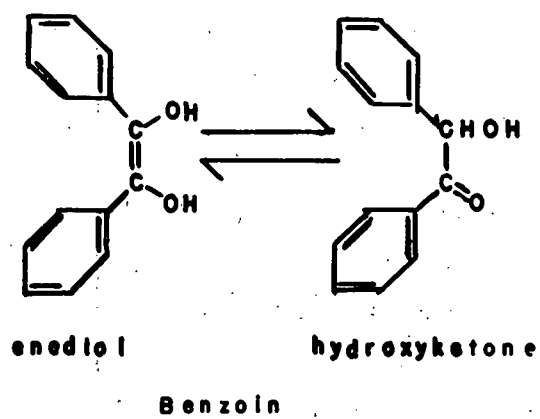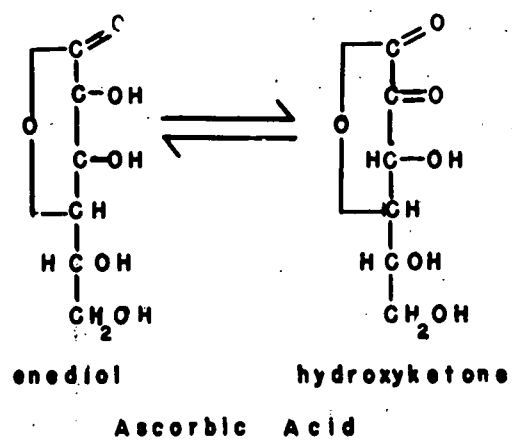
enediol   hydroxyketone

Ascorbic   Acid

enediol   hydroxyketone

Benzoin

Fig. 5

When benzene was the solvent, no marked rise occurred in the chlorin band at 618 mμ, but a new band appeared at 602 mμ, and strengthened rapidly as the porphin band at 550 mμ faded. This reaction was faster than the reaction in pyridine, the porphin being mostly reduced in twenty minutes of sunlight, as compared to about an hour when pyridine was used. Because it was formed by a reducing agent directly after chlorin (dihydroporphin), the compound characterized by bands at 606 mμ in basic solution and 602 in benzene solution was called zinc tetrahydrotetraphenylporphin. Other evidence in support of this identification is provided later.

When ethyl alcohol was used as solvent, the results were intermediate between those with benzene and pyridine. A reaction run in piperidine as solvent hardly went at all; only a little chlorin was eventually formed. Trials of other solvents-- dioxane, morpholine, pyrrole, collidine-- showed that the stronger the base the slower the reaction, and the more the chlorin formed. Apparently zinc chlorin is stabilized to reduction by complexing with base comparatively more than zinc porphin is.

When reactions were run in benzene solution containing 1/2% piperidine, two new phenomena were uncovered. Since the solvent was mostly benzene, the reaction rate was fast, but since the porphin was all complexed by the strong base, considerable chlorin was produced. At the start of the reaction, a sharp peak rose at 457 mμ, whose extinction coefficient was later found to be about 150,000. This peak only appears when reduction is occurring or about to occur, and is only seen when benzoin is the reducing agent.

The other event was the appearance, toward the end of the reaction, of a new band at 642 mμ. This band rose as the tetrahydroporphin band fell, but after the tube was opened to the air and allowed to stand overnight, the 642-mμ band had disappeared, regenerating the characteristic spectrum of zinc tetrahydrotetraphenylporphin. Therefore this new compound is tentatively identified as zinc hexahydrotetraphenylporphin, the third hydrogenation product of zinc tetraphenylporphin. Further discussion of this identification is presented in the last section, when structure and properties of hexahydroporphin are discussed.

A number of reducing agents were examined, to see which ones would affect zinc porphin. Ascorbic acid was tried again, this time in alcoholic solution and in alcohol containing a little pyridine. In both cases, after ten or so hours of sunlight, reduction was detected, with formation of zinc chlorin and tetrahydroporphin. Again, addition of pyridine produced larger yields of zinc chlorin.

Photoreduction of Zinc Tetraphenylporphin

by Benzoin in Benzene
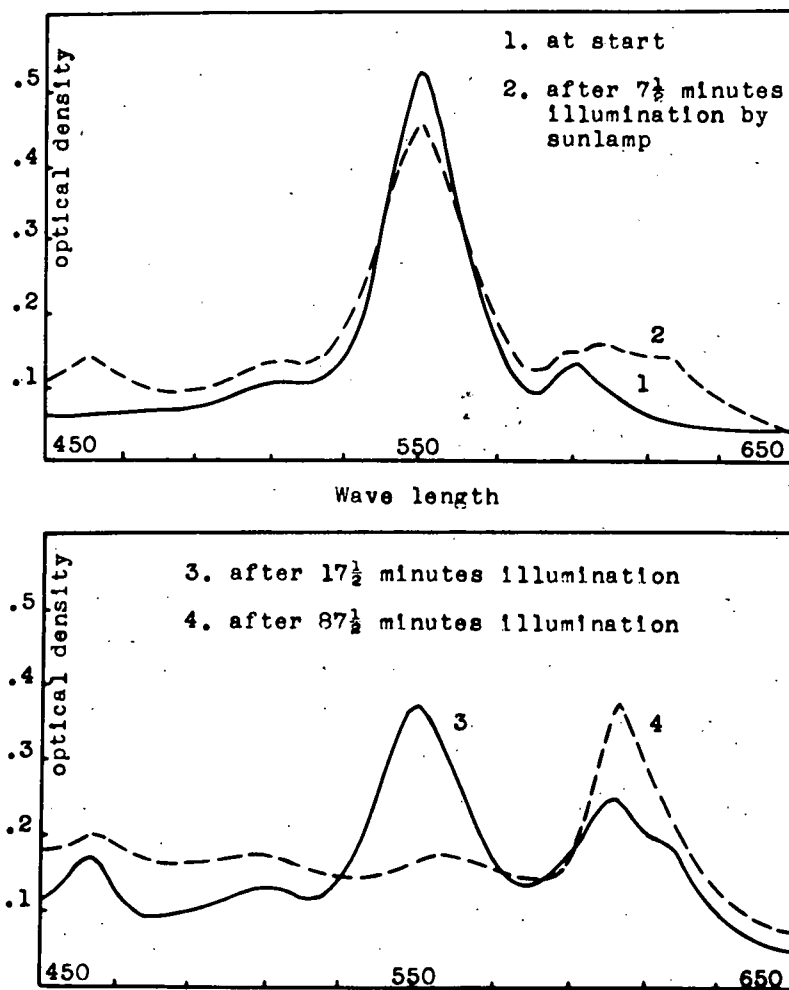
Run XI of Table VIII

Fig. 6

Dihydroxyacetone was found to be a very useful reducing agent. Although the reaction, when alcohol alone is the solvent, is extremely slow, when a base such as pyridine is added, reduction through the chlorin to the tetrahydroporphin is complete after two hours of sunlight. In parallel runs, a tube with solvent 1/3 pyridine and 2/3 alcohol showed complete reduction to tetrahydroporphin in two hours, whereas a tube containing just enough pyridine to half complex the porphin showed that reduction had barely started in that time. Notable is the high yield of zinc tetrahydroporphin obtainable by this method: a yield of about 60 percent was obtained after one hour's sunlight, the solvent being alcohol containing 1/2 percent piperidine. It would appear that it is harder to reduce the tetrahydroporphin than zinc porphin itself, and that when all porphyrins are complexed with a strong base, dihydroxyacetone is able to reduce zinc porphin and chlorin, but almost unable to reduce tetrahydroporphin.

This reaction provides a means of obtaining solutions of zinc tetrahydroporphin free from reducing agents, for use in experiments on reverse oxidation and for obtaining spectra. To the solution from the reaction, benzene is added; the mixture is then extracted about fifteen times with water to remove alcohol, pyridine, and dihydroxyacetone, leaving behind a solution of zinc tetrahydroporphin in benzene. When once the reaction vessel is opened, all work must be done in near darkness, for the tetrahydroporphin is extremely susceptible to destruction by oxygen in the presence of light. Even in the dark, a solution of zinc tetrahydroporphin is decomposed by oxygen, on standing for about a week, with regeneration of small amounts of zinc chlorin. An attempt to chromatograph the tetrahydroporphin failed; all that could be isolated from the column was a small amount of chlorin.

That the reduction of dihydroxyacetone is promoted by bases is in contrast to the hindrance by bases of reduction by benzoin. Perhaps it is only the enediol form of dihydroxyacetone that is active, while dihydroxyacetone normally exists only in the keto form; base might then function by catalyzing conversion of the keto form to the active enediol form. A crude preparation of reductone[13] and some not very pure dioxymaleic acid, both compounds that resemble dihydroxyacetone, showed behavior similar to that of dihydroxyacetone.

Two other biochemical reducing agents were tried without success. These were malic acid and citric acid. Tartronic acid[34] was also tried, but failed to produce any reduction. In view of the fact that benzoquinone oxidizes zinc chlorin readily, it is not surprising that hydroquinone showed no reducing action on zinc porphin.

Fig. 7

Sketch of Spectrum of Zinc Hexahydroporphin in
Benzene + ½% Piperidine

$\epsilon \approx 6.0 \times 10^3$

Fig. 8

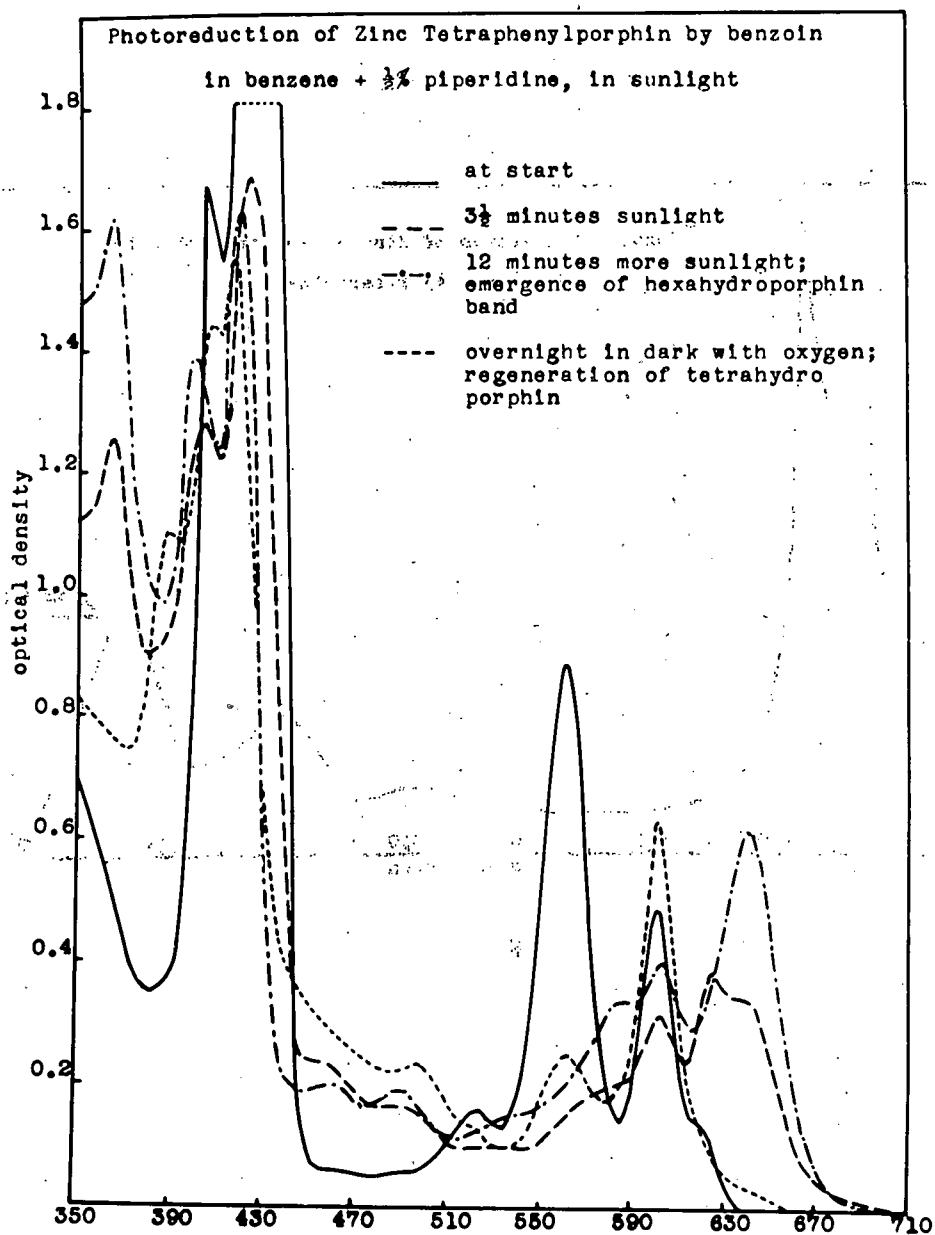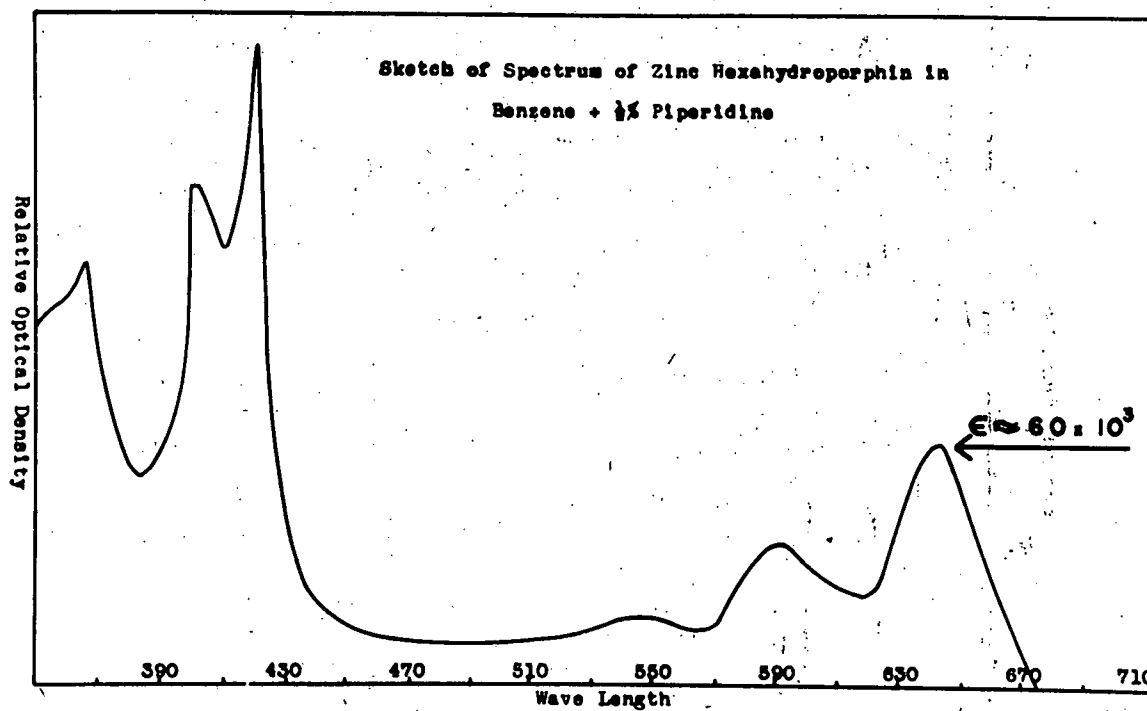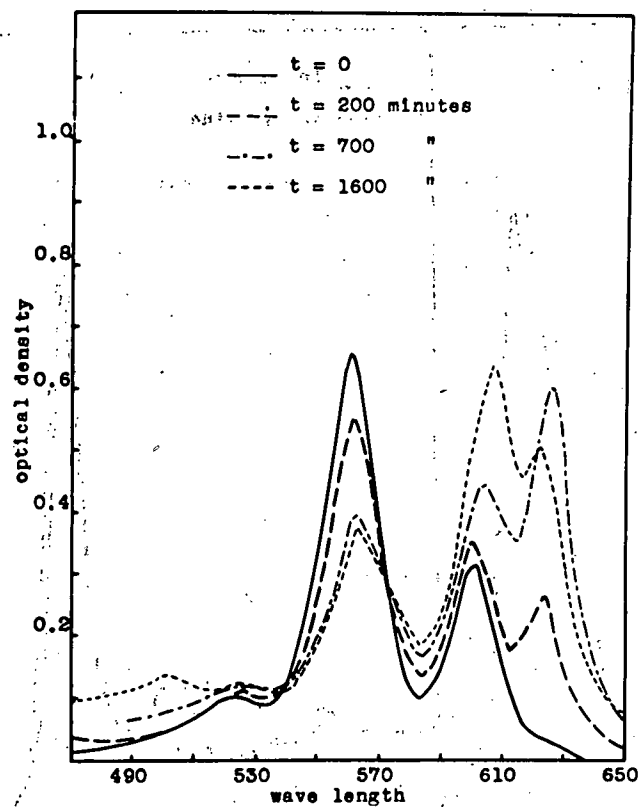Photoreduction of Zinc Tetraphenylporphin

by Dihydroxyacetone

Solvent: 30% pyridine, 70% alcohol

G. E. RSP2 Spotlight, (incandescent)

Fig 9

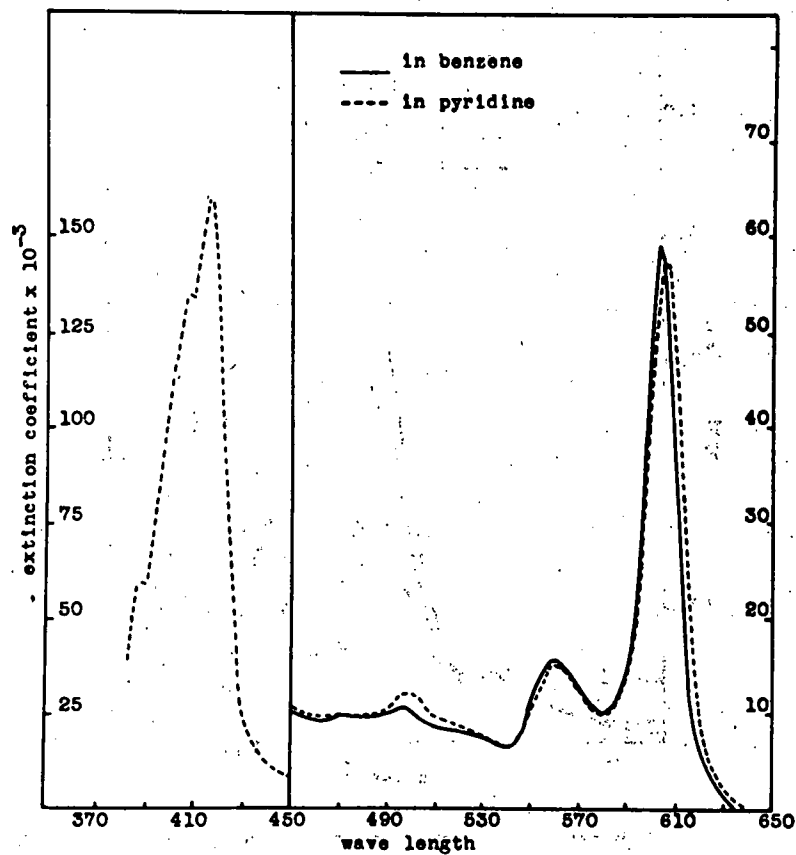Spectra of Zinc Tetrahydrotetraphenylporphin

Fig. 10. We lack a satisfactory tracing of the Soret band in Benzene, but it appears to be almost identical with that in pyridine; see also Fig. 5 in: G. D. Dorough, J. R. Miller, J. A. C. S. 74: 6106, (1952).

Since a sugar, arabinose for example, contains a latent aldehyde group, it also contains a latent enediol group, and might permit slow reduction. With pyridine as solvent, several days of sunshine did produce a faint band of zinc chlorin at 623 mμ.

Analogous to the enediols are the hydrazines. It has already been pointed out in the introduction that phenylhydrazine and hydrazobenzene are able to reduce zinc porphin. Hydrazobenzene's ability has been confirmed, and semicarbazide has also been found active. However, neither of these agents seems able to bring the reaction to completion, even after several days of sunlight. 2,4-Dinitrophenyl-hydrazine did not affect zinc porphin during four hours of sunlight.

In view of the importance of the thiol-disulfide couple in biochemistry, and especially its proposed role in photosynthesis,[6] attempts were made to reduce zinc porphin by mercaptans. N-hexyl mercaptan and 1,2-ethanedithiol, in benzene solution, or in benzene containing pyridine, gave evidence of formation of zinc chlorin on prolonged exposure to sunlight. These reductions with thiols are, if anything, slower than reductions with hydrazines, and are certainly not complete.

One other benzoin was tried; that is the paradimethylaminobenzoin $(CH_3)_2NC_6H_4COCHOHC_6H_5$.[44] This agent is about as fast as benzoin itself, reducing zinc porphin to chlorin and tetrahydroporphin in a solution of benzene plus pyridine.

Oxidations of Tetrahydroporphins

Up to now we have assumed that the reduction product with band at 602 mμ is zinc tetrahydroporphin, but without citing proof other than its method of formation. An accurate carbon-hydrogen analysis would clearly decide; however, because of the small amount of compound available, and its extreme sensitivity to oxygen, making it difficult to purify, the analysis has not been done in this laboratory.

We already know that chlorins (dihydroporphins) are oxidized by quinones to porphins, as has been described in the introduction. It might be expected, therefore, that zinc tetrahydroporphin would be oxidized by quinones to chlorin and a porphin. This has indeed been shown to be the case. With 1,2-naptha-quinone or 9,10-phenanthraquinone as oxidizing agent, and preparations of pure zinc tetrahydroporphin prepared by reduction of dihydroxyacetone, smooth and probably quantitative conversion to zinc porphin was obtained. When a solution containing both zinc tetrahydroporphin and zinc chlorin was oxidized, the chlorin was oxidized much more rapidly, explaining why no chlorin is observed as intermediate in oxidation of zinc tetrahydroporphin.

The susceptibility of zinc tetrahydroporphin to oxygen has been referred to; mostly decomposition into unrecognizable products occurs, but usually a little chlorin can be detected. Zinc chlorin is easily identified in small amounts by the sharp peak at 623 mμ and the Soret band at 420 mμ. Oxidation is especially rapid on a chromatographic column; apparently the surface of adsorbent particles catalyzes it. When zinc tetrahydroporphin and chlorin are chromatographed together on magnesia, chlorin forms the upper band, tetrahydroporphin the lower, but this band spreads and disintegrates even while being developed. All that can be eluted from the column is zinc chlorin. Enhancement of chlorin concentration has also been observed in zinc tetrahydroporphin solutions that have stood open to the air in the dark for a week. Free base tetrahydroporphin, which may be made by washing the zinc complex with hydrochloric acid and ammonia, exhibits enhancement of free base chlorin concentration after standing open to air for five days. The free base tetrahydroporphin is almost all destroyed in this time. It is convenient to exhibit in the form of a chart the relationships between the zinc complexes of porphin, chlorin, tetrahydroporphin, and hexahydroporphin.

Photoreduction in Other Systems

Krasnovskii and his associates, in a series of articles, have reported photo-reductions of chlorophyll, magnesium phthalocyanine, and other compounds by reducing agents such as ascorbic acid), which reverse on standing in the dark, more rapidly if oxygen is present.[23-28] We have not tried systematically to check this work, but have tried to reproduce some of it. Magnesium phthalocyanine[*] does not seem to be affected by ascorbic acid in pyridine and sunlight, despite Krasnovskii's claim of quick reduction and quick reversal.[27] The structure of phthalocyanine shows no points susceptible to hydrogenation. Krasnovskii, photoreducing chlorophyll with ascorbic acid, notes buildup of a compound with one absorption band at 520 mμ, which in the dark reverts to chlorophyll.[28] Photoreducing chlorophyll[**] with dihydroxyacetone in pyridine plus alcohol, we noticed first the emergence of a band at 520 mμ, which on standing in the dark disappeared, but apparently without regeneration of chlorophyll. The position and shape of this band reported by Krasnovskii suggests that it is an oxidatively destroyed compound of shlorophyll, similar to those reported in the next section, and we prefer this interpretation. Later in the run (apparently when all the oxygen is used up), a band emerges at 616 mμ, which from its position and sharpness, we

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[*] We are grateful to Mr. Mark Krakov, who prepared this compound as a special project in an organic chemistry course.

[**] Very kindly supplied for this experiment by Dr. Andrew Benson.

Redox Relations among the Zinc Tetraphenylporphyrins

```
                  Benzoin or Dihydroxyacetone, base; light;
 ┌───────────┐          variable yield              ┌───────────┐
 │  PORPHIN  │ ──────────────────────────────────→ │  CHLORIN  │
 │           │ ←──────────────────────────────────  │           │
 └───────────┘    Quinones;  light;  high yield      └───────────┘

       Quinones;  light;  high yield        Oxygen; dark;  low yield


  Benzoin, no base;  light      ┌─────────────────────┐  Benzoin or Dihydroxyacetone;
         low yield          ──→ │ TETRAHYDROPORPHIN   │ ←  light;  high yield
                               └─────────────────────┘

  Oxygen;  dark;  high yield         Benzoin, benzene + ½% piperidine;
                                          light;  variable yield


                        ┌───────────────────┐
                        │ HEXAHYDROPORPHIN  │ ←
                        └───────────────────┘
```
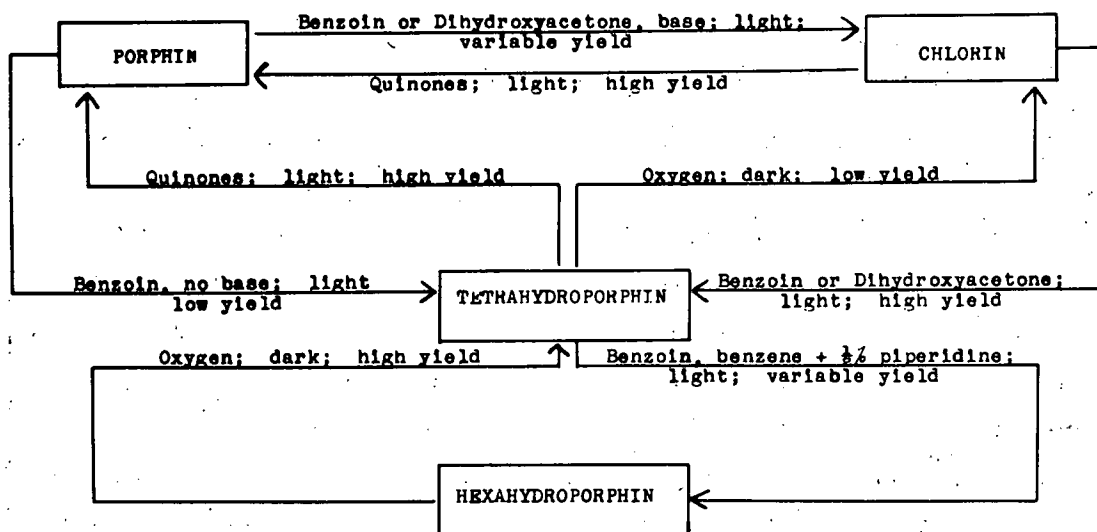
Fig. 11

suggest is analogous to our tetrahydroporphin. There is no sign of reversal before admission of oxygen, but afterwards, slow dark reversal to chlorophyll, or at least to a compound having a band at the same place (660 mμ), occurs. Reduction of chlorophyll seems, then, to fall into the scheme we have outlined.

It is not the purpose of this thesis to enter into an evaluation of Krasnovskii's work. He may have been using much higher light intensities than sunlight, or significantly different reaction conditions, especially with regard to oxygen concentration, and may have been reporting phenomena essentially different from those we have observed.

Destructive Oxidation of Zinc Tetraphenylporphin

Steps were taken from the beginning to exclude oxygen from the reaction tubes, for it is known that chlorins are very susceptible to photochemical destruction by oxygen,[21] and we wished to detect reduction by the appearance of chlorin. If oxygen is, however, accidentally or purposely present, the result is usually what one would expect: the porphin bands fade until the oxygen is used up at about the rate at which reduction would proceed, without production of any identifiable compound.

With benzoin and oxygen, the situation is quite different. It has long been recognized that zinc porphin, in the presence of light and air, is slowly destroyed, yielding at first some unidentified visibly colored products that are eventually converted to colorless products, with bleaching of the contents of the tube. The process requires several days of sunlight. The product or products first formed have one absorption band whose peak is poorly defined and varies from 490 to 500 mμ. When benzoin and oxygen are both present, however, destruction of porphyrin is very rapid, and the product generally has its peak absorption at 530 in benzene, or 510 in pyridine. These compounds are also apparently susceptible to benzoin and oxygen in the light, for they are soon destroyed, leaving a colorless solution. These oxidation products seem to be fairly stable in the dark, but are sensitive to acid, which converts them to compounds having a general and bandless absorption in the blue. The nature of these compounds is not apparent; nor do we have any idea how many we are dealing with.

It was latterly discovered that if one allows a partially oxidized solution of zinc porphin in benzene, without benzoin, to stand in the dark for several days, the initial oxidation product with band at 490 mμ is converted into a blue compound with its highest peak at 628 mμ. The concentration of this blue compound may be built up by alternately exposing the tube to sunlight under a yellow filter and allowing it to stand in the dark, for the blue compound is not very sensitive to light.

This compound is apparently not formed in any great quantity when the oxidation is catalyzed by benzoin, or it would surely have been found earlier. If a drop of pyridine is added to a benzene solution of this compound, the solution becomes slightly greener, and the high-absorption band moves from 628 to 632 mμ. The compound is stable to 3-$\underline{N}$ hydrochloric acid, but 6-$\underline{N}$ HCl liberates the zinc, forming a free base with a beautiful purple color, having two bands -- one in the yellow and the other in the green. This free base is stable to concentrated ammonia and potassium hydroxide. If the free base in dry benzene is treated with a solution of zinc acetate in pyridine, the pyridinate of the zinc complex is formed, and the band at 632 mμ returns. Judging from the ease with which it forms metal complexes, the compound must still have a cyclic structure, but the absence of a definite Soret band indicates that perhaps one of the bridge carbons has been attacked by oxygen. The spectra of these and some other oxidation products of porphin are illustrated.

It was soon found that benzil shares with benzoin the ability to catalyze the oxidation of zinc porphin, forming a compound with maximum absorption at about 500 mμ. Since benzil has no conceivable ability to hydrogenate, this reaction is apparently separate from the hydrogenation. This is further borne out by the discovery that many other compounds were able to mediate the destruction of zinc porphin in air and sunlight: acetophenone, benzaldehyde, desoxybenzoin, butyl phenylketone, p-dimethyl aminobenzoin, anthracene, phenanthraquinone, and possibly some mercaptans. Unable to catalyze the oxidation were benzophenone, napthalene, diphenyl disulfide, and p-azoanisole. The spectra of the oxidation products in each case were not recorded, but often no red compound absorbing near 500 mμ occurred -- only a fading of porphin bands. In the case of acetophenone, the compound was red, as with benzoin. The destruction in the presence of benzaldehyde was particularly rapid and complete, but the auto-oxidation of benzaldehyde may be entering into the reaction. The solution after destruction in the presence of anthracene was yellow; it is to be noted that napthalene neither helps nor hinders the reaction. The rate of destruction was much smaller when p-dimethylaminobenzoin was used than it is with benzoin. Many of the effective compounds have a COC_6H_5 group, but benzophenone is quite ineffective.

Magnesium phthalocyanine, which bleaches slowly in air and light, bleaches very rapidly when benzoin is added. This is evidently an analogous reaction.

The cause of the sharp, intense absorption band that appears during benzoin reductions at 457 mμ in the presence of base, and 463 mμ in benzene, remains unknown. Since it only occurs when a trace of oxygen is present, it may represent the first stage in oxidative destruction of porphin, and be very sensitive

to extra oxygen. Since it only occurs when reduction is about to take place, it may be that benzoin reduces porphin to a semiquinone-type radical, which then reacts with oxygen. Unfortunately, no bands of the same compound to the red side of that sharp peak have been found; this is curious if the peak really corresponds to a Soret band, for the spectra are good enough to show evidence of even a small band in the red or green part.

The copper and nickel complexes of porphin are as susceptible to destructive oxidation as is the zinc complex, although they are reduced at only 1/10 the speed of reduction of zinc complex.

It might be emphasized that the rate of oxidative destruction by benzoin and oxygen is faster than the sum of the rate of reduction by benzoin alone and the rate of destruction by oxygen alone; five or ten minutes of sunlight suffices for complete destruction.

The intent of this work is to study the rate of reduction of zinc porphyrin by some convenient agent. All reductions encountered so far, save that by the benzoins, are inconveniently slow. We therefore decided that, in spite of its side reactions, the reduction by benzoin must be the one to be explored. Benzoin may be purified by recrystallization from aqueous alcohol, and is stable indefinitely.

Destructive Oxidation of Zinc Tetraphenylporphin

Catalysed by Benzoin

Light Source: AH-4 Mercury Lamp

Fig. 12

Reaction of Zinc Tetraphenylporphin with Oxygen

in Benzene Solution
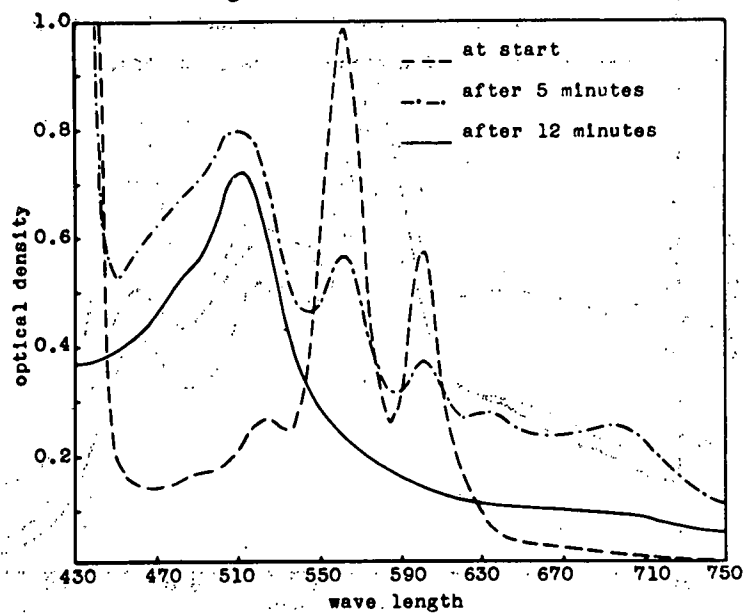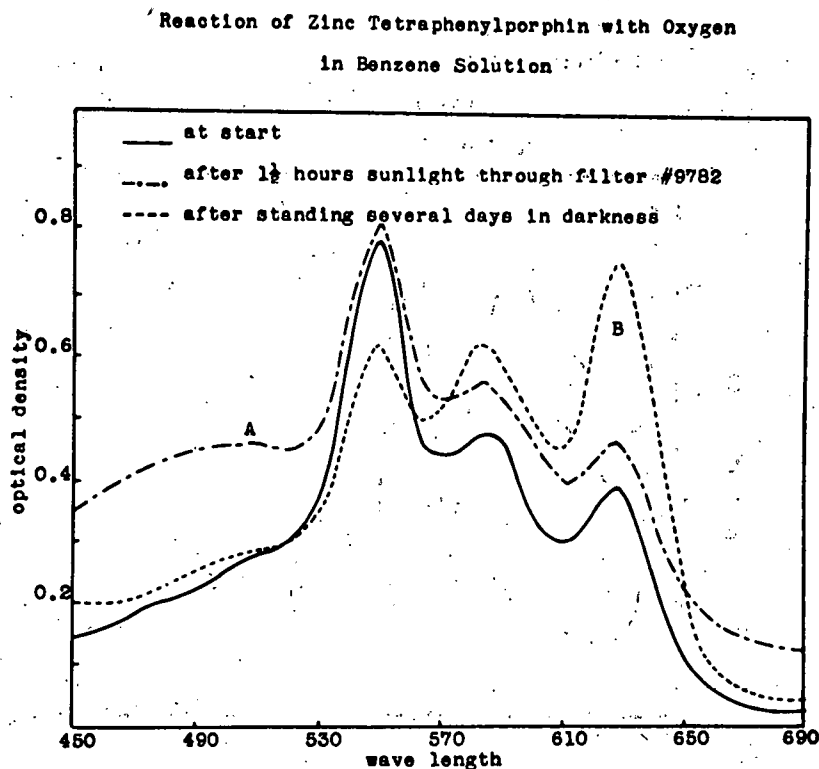

Fig. 13. At start, the porphin has already been partially destroyed.
Irradiation brings about buildup of first degradation products
at A. Standing in the dark, these change into a product with
band at B.

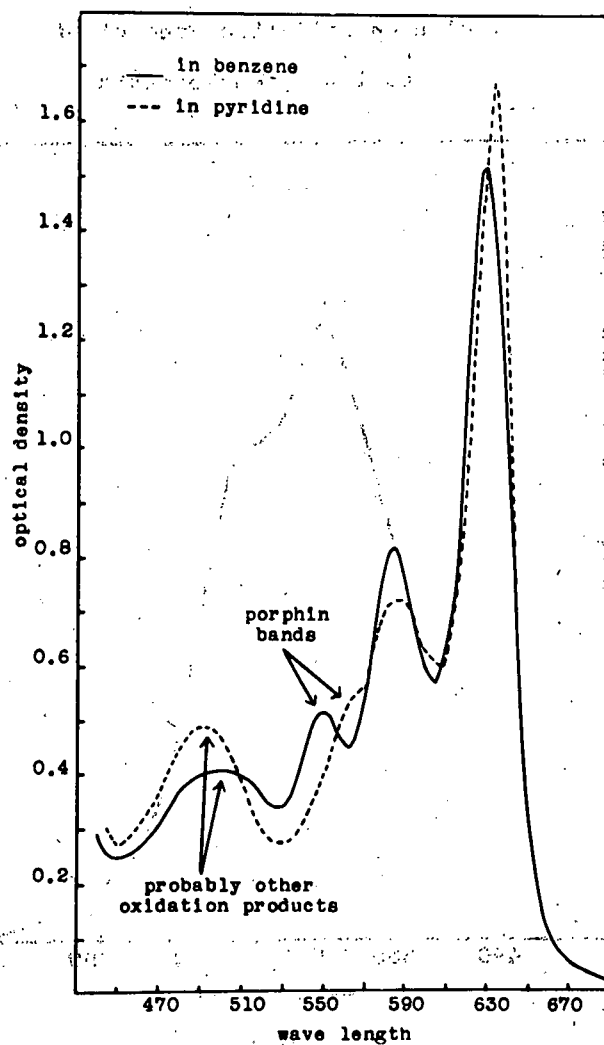Spectra of Blue Oxidation Product

of Zinc Tetraphenylporphin

Fig. 14

Spectrum of Free Base
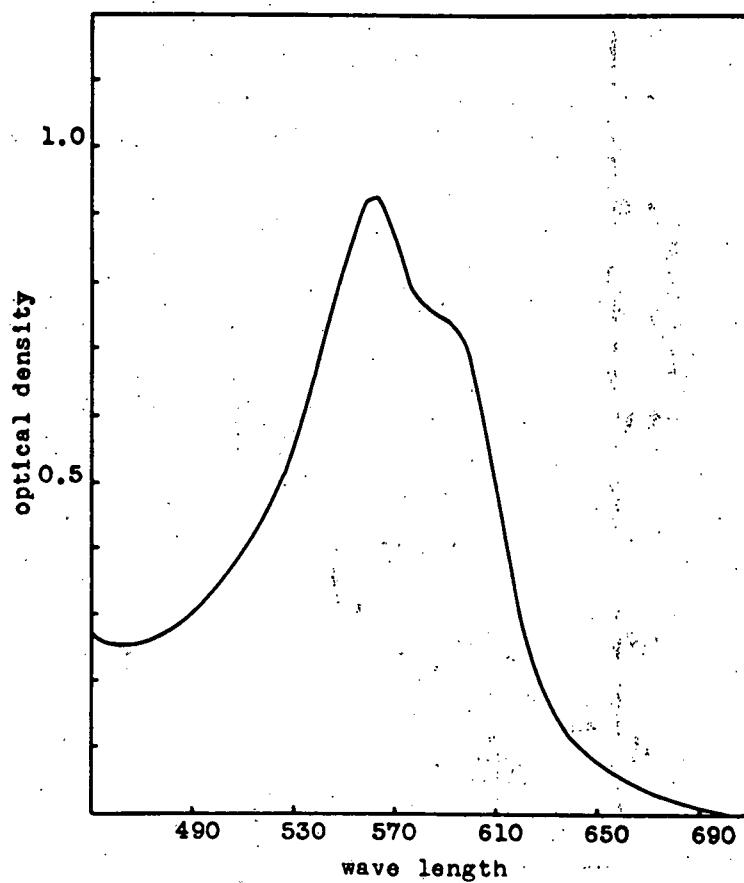
of Blue Oxidation Product of

Zinc Tetraphenylporphin

Fig. 15

KINETICS OF THE PHOTOCHEMICAL REDUCTION
OF ZINC TETRAPHENYLPORPHIN BY BENZOIN

Apparatus and Procedure

The zinc tetraphenylporphin used for quantitative rate runs was chromatographed by the procedure described, and stock solutions were made up in benzene; these are kept in the dark to avoid decomposition. A stock solution of benzoin was also made up, but often benzoin was weighed out directly before using. For an average run, 1 cc. of zinc porphin solution (ca. 1.4×10^{-7} moles) and 5 mg of benzoin are washed into one of the square tubes with enough benzene to fill the tube. The height of the meniscus is measured in centimeters; a minor correction then gives the volume of solution in cubic cemtimeters. A spectrum is taken on the Cary recording spectrophotometer, from which the porphin concentration may be obtained. The tube is now placed in water heated by a hot plate almost to the boiling point of benzene, 80°, and the contents are flushed by a stream of purified nitrogen until about one fourth of the solvent has been evaporated. While a stream of nitrogen is still running through, the bath water is cooled with ice, and the joint of the tube is greased with Dow-Corning high-vacuum silicone grease. As quickly as possible, the tube is joined to the head, the top of which is connected to a vacuum pump through a piece of tygon tubing. The tube is evacuated, with shaking to boil the benzene, until the volume of solution left in the tube is between 2-1/2 and 3 cc. The tygon is then sealed off with hot crucible tongs, thus insuring a vacuum in the upper part of the head, and helping prevent leakage of air through the stopcock of the head. The tube, with head, is then removed from the evacuation line.

Another spectrum is taken, to obtain the new porphin concentration, and from it, the new benzoin concentration. The volume of the solution is measured. All work so far has been carried out in a dimly lighted room. For irradiation, the tube is now placed in a jacket that is part of a thermostat by which the temperature may be held at from 24° to 25°. A General Electric 275-watt Reflector Sunlamp of known energy distribution is turned on, filters may be interposed if desired, and irridiation is begun. Spectra are taken at convenient intervals; the light flux through the tube is measured by a bolometer.

From the series of spectra obtained, optical densities at various wave lengths may be used to find the concentrations of porphin, chlorin, tetrahydroporphin, and whatever else is present in the solution.

The tubes used are made from pyrex glass available from Fischer and Porter Co., Hatboro, Pennsylvania, in the form of 4 in. lengths. The tubing is of square cross section, and has two opposite sides polished optically flat. The inside width of the tubing is 0.96 cm. One end of a piece of this tubing is sealed flat; the other is connected to a 10/40 male ground-glass joint. The volume of the tube thus formed, below the joint, is 4.5 to 5.5 cc.

A head is simply a female 10/40 joint connected to a small stopcock, which in turn is connected to a male 10/40 joint. The tygon tubing fits snugly over this joint.

Tank nitrogen is purified of the last traces of oxygen by passing it through a train of wash bottles. The gas is first bubbled through two wash bottles containing Fieser's solution, which is an alkaline solution of sodium hydrosulfite and sodium beta-napthaquinone sulfonate.[15] After passing through a tube containing Drierite, the gas is washed by a solution of the sodium ketil of benzophenone, made by dissolving benzophenone and sodium-potassium alloy in toluene, following directions of Fieser.[15] The ketil solution is protected from air by a final wash bottle containing white oil(Standard). Connected to this last bottle is a capillary, which is inserted into the solution to be flushed.

Most of the energy produced by the sunlamp is contained in a few mercury lines; there is a weak continuous spectrum in the red and infra-red. The energy emitted in the principal lines was determined with the use of filters and the bolometer. The distribution of energy output among the mercury lines under operating conditions is listed in the table below.

TABLE II
Distribution of Energy of G. E. Reflector Sunlamp

Wavelength of line, mμ	Percent of total energy output
longer than 622	19. 5%
622	3. 2
576	22. 7
545	22. 3
436	15. 2
405	6. 9
365	7. 6
	97. 4%

The spectra of the filters that have been found to be most useful are shown, together with their Corning catalogue number. The uses for the several filters appear in the discussion of results.

The procedure for finding the distribution of energy among the mercury lines may be briefly indicated. Filter No. 2403 passes the far red and infrared lines and continuum only. Filter No. 2412 passes these and also the 622 mμ line. A didymium filter, No. 5120, spectrum not shown, can be used to block completely the yellow mercury line at 576 mμ. Use of filters No. 5120 and No. 3480 together gives a check on the energy in the red lines. In addition to the red lines, filters No. 5120 and No. 3385 together pass the green line at 545 mμ. Filter No. 3385 alone passes also the yellow line at 576 mμ. Either filter No. 5874 or 5970 may be used to isolate the 365 mμ line. The use of filter No. 9872 with and without No. 3385 permits isolation of the line at 492 mμ; it is found to contain very little energy. The only lines now unknown are at 405 and 436 mμ; use of filters No. 5120 and 9872 separately permits setting up simultaneous equations for the energies in these two lines.

Corning Sharp Cut-Off Filters

Fig. 16

Corning Blue Passing Filters
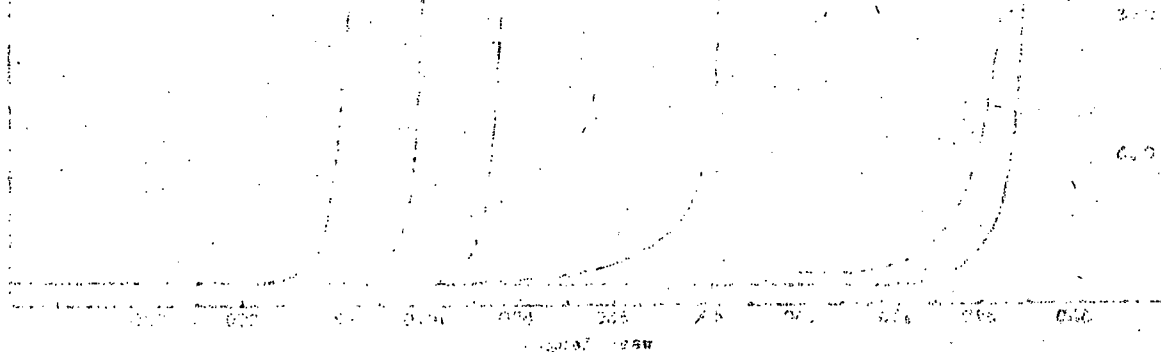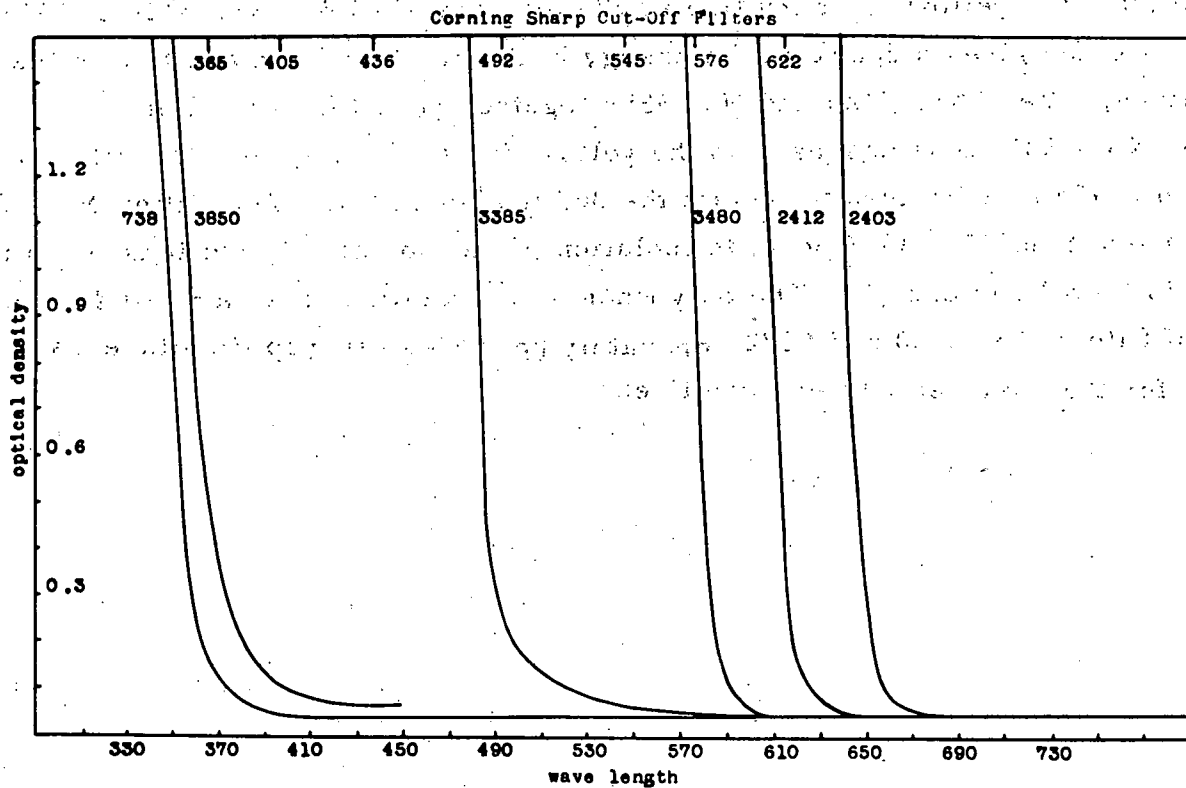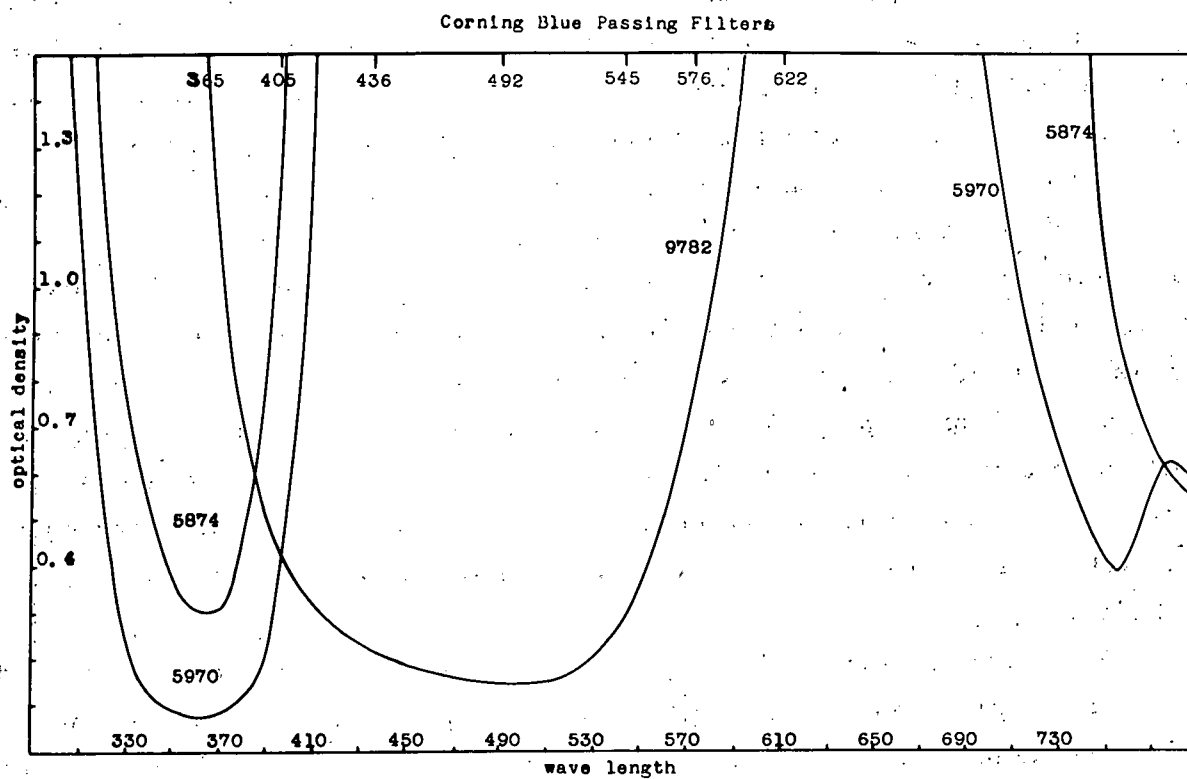

Fig. 17

A diagram of the apparatus for irradiating the tube is given in Fig. 18. Light from the sunlamp (A) passes through a lucite tank (B) (through which water is circulated) containing a piece of infra red absorbing glass (C). The cooled light then passes through the circular aperture into a box (D). Filters may be placed directly behind the aperture (E). At the far end of the box is a stage on which the bolometer is set when in use. In the box the diverging beam of light from the lamp encounters a large condensing lens (F), which focuses an image of the aperture onto the sensitive surface of the bolometer (J). All light passing through the aperture is received by the bolometer, which has a sensitive area of 13 sq. cm. Between the lens and the bolometer is the jacket (H) in which the reaction tube (I) is placed. A bakelite diaphragm (G) with a rectangular opening assures that all light passing through it passes also through the solution into the tube and is received on the surface of the bolometer.

The temperature of the distilled water that circulates through the jacket containing the reaction tube is controlled by a Fenwal thermostat (O), immersed in a pail of water (K) below the box, from which the water is pumped by a "Fountainette" pump (N) up to the jacket. Heat is supplied by a "Calrod" heating element (L) controlled by a "Variac" transformer (P). Sometimes cooling is required to maintain the temperature near 24° C. Tap water circulates through a copper coil (M) immersed in the pail before passing to the tank containing the infrared glass.

For the assembly and calibration of the bolometer we are deeply indebted to Dr. Peter Massini, who is currently at the Philips Research Laboratories, Eindhoven, Holland. The instrument is a Kurlbaum large-area bolometer, and is used with an auto battery, a Leeds and Northrup galvanometer, and a resistance box assembled by Dr. Massini. Its wiring diagram is illustrated. Calibration was carried out with a lamp furnished by the National Bureau of Standards as a radiation standard. The results of the calibration are also tabulated. The "Flux" column may be obtained from the "intensity" column by multiplying by the area of receiving surface, 13 sq. cm.

The shape and height of the reaction tubes plus heads made necessary the construction of auxiliary equipment in order to accommodate them on the Cary spectrophotometer. We are most grateful to Mr. Paul Hayes, under whose direction this equipment was constructed.
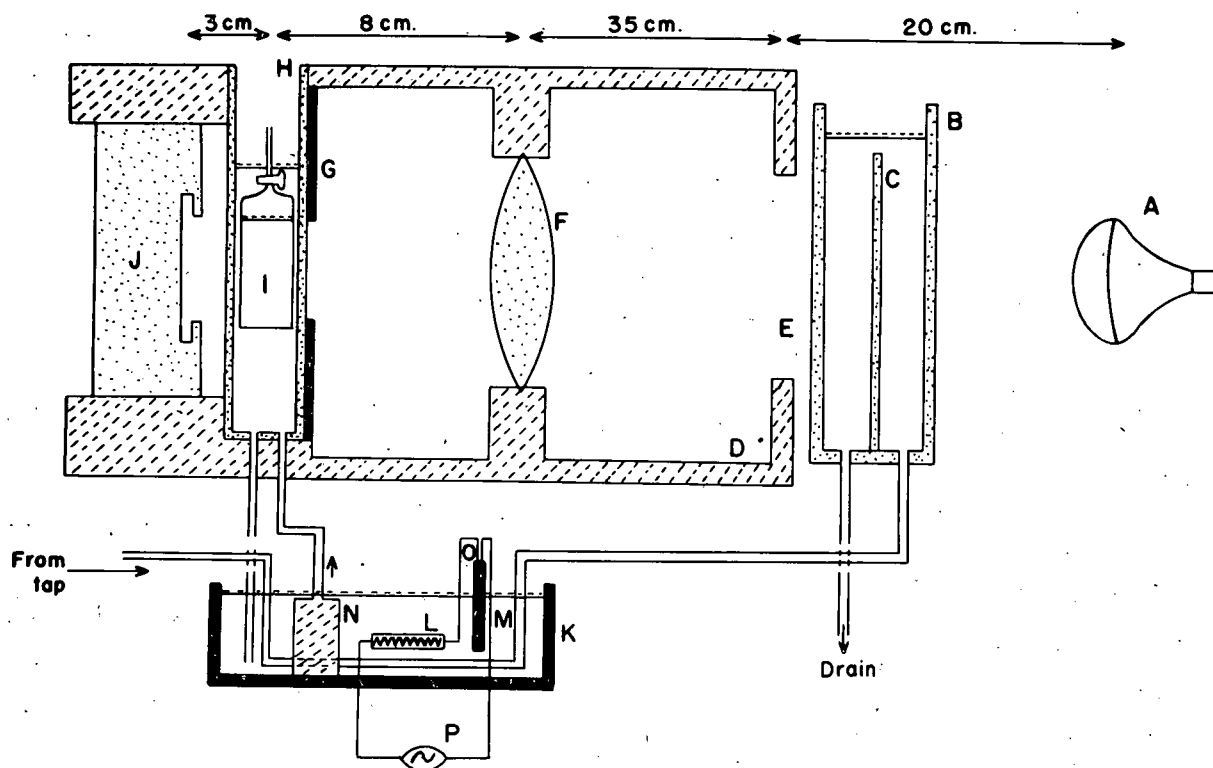
Fig. 18

Key to Fig. 18

A. G. E. 275-watt reflector sunlamp
B. Lucite tank with water
C. Infra-red absorbing glass
D. Irradiation box
E. Aperture
F. Condensing lens
G. Diaphragm
H. Jacket with thermostatted water

I. Reaction tube
J. Bolometer
K. Reservoir of thermostat
L. Calrod for heating
M. Copper coil, with tap
   water for cooling
N. "Fountainette" pump
O. Fenwal thermostat

P. Variac transformer

Chronology of the Experiments

Before discussing the results of the rate runs using benzoin as reducing agent, it will be necessary to review the state of our knowledge at the commencement of these runs. We expected that the mechanism of reduction of porphin would be essentially the same as oxidation of chlorin, that is, a porphin molecule in the triplet excited state would react with a molecule of benzoin, and as a consequence the rate would be proportional to the amount of light absorbed by the porphin, but independent of the benzoin concentration.

This latter consequence, dependence upon benzoin concentration, was made the first object of research in the series of rate runs. Verification of the former consequence, dependence on light absorbed by the porphin, had by no means been neglected in the qualitative work, but no particular conclusions could be drawn except that it appeared that the reaction did not go when light of the long-wavelength visible bands of porphin was employed. The lack of definitive results must be attributed to the facts that the light sources were not calibrated, that unknown error was introduced by traces of oxygen, and that unexpected inhibitions of the reaction may have occurred.

It was discovered, early in the experiments, that amounts of benzil comparable to the amount of benzoin inhibited the reaction completely. In one experiment, porphin was partly reduced to chlorin and tetrahydroporphin, then benzil was added. On further irradiation, no appreciable change was observed in any of the characteristic bands. In the course of experiments on the effect of base on the reaction, it was discovered that quinoline almost prevents reaction in sunlight, although it is quite a weak base. The presence of quinoline also slows considerably degradative oxidation by benzoin, air, and light. Piperidine, a strong base, will, if present in sufficient quantity, prevent reduction by benzoin, but will not prevent the degradative oxidation. A third case of inhibition was discovered by accident. When one tube of porphin and benzoin obstinately refused to react, the trouble was traced to Apiezon N stopcock grease that had dissolved out of the stopcock into the solution. The grease, which was yellow, was replaced by colorless high-vacuum silicone grease in all subsequent experiments. The cause of these inhibitions was at the time unknown.

The first rate run tested whether light absorbed by the long-wave bands of porphin was effective. For alternate 25-minute periods, filter No. 3385 was imposed and removed from the light path. This filter passes only light of the long-wavelength bands of porphin, that is, longer than 490 mμ. The accompanying graph shows the fall in the porphin band, as a function of time and kind of light. The solution contained pyridine. Clearly, no measurable amount of

WIRING DIAGRAM
FOR BOLOMETER
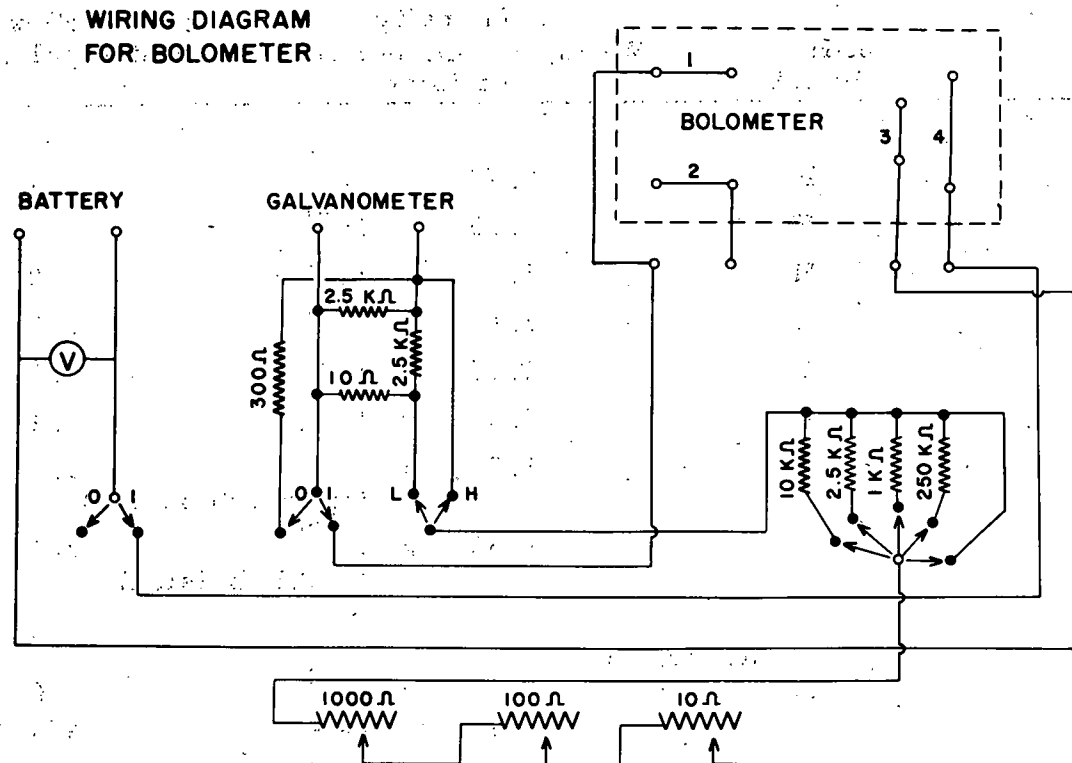
Fig. 19

Table III

Calibration of Bolometer

Range Selector Position	L-H Switch	Intensity Watts/sq. cm. per Galv. division		Flux Watts/galv. division
1	H	6.7	$\times 10^{-6}$	8.7 $\times 10^{-5}$
2	H	2.25	$\times 10^{-5}$	2.9 $\times 10^{-4}$
3	H	5.4	$\times 10^{-5}$	7.0 $\times 10^{-4}$
4	H	2.1	$\times 10^{-4}$	2.7 $\times 10^{-3}$
5	L	1.55	$\times 10^{-3}$	2.0 $\times 10^{-2}$
6	L	5.45	$\times 10^{-3}$	7.1 $\times 10^{-2}$
7	L	1.3	$\times 10^{-2}$ (up to 4 divisions)	1.7 $\times 10^{-1}$
		1.65	$\times 10^{-2}$ (at 8th division)	2.15 $\times 10^{-1}$
8	L	at division 0.75	4.3 $\times 10^{-2}$	5.6 $\times 10^{-1}$
		2.3	5.5 $\times 10^{-2}$	7.2 $\times 10^{-1}$
		5.3	9.6 $\times 10^{-2}$	12.5 $\times 10^{-1}$

For battery voltage: 4.3 v.

Area of receiving surface: 13.0 cm^2

The galvanometer (Leeds and Northrup) has

10 divisions on its scale

reduction results from exposure to yellow light.[*] The light source used for this experiment was an RSP2 spotlight, incandescent, with a great deal more energy in the green region than in the violet.

Two reasonable alternatives now confronted us: either light received in the Soret (400 mμ) band of the porphin was active, whereas green light was inactive; or light received by benzoin alone is responsible. Now, 30 percent of the energy put out by the sunlamp lies in the three mercury lines 4358 Å, 4045 Å, and 3650 Å. Benzoin absorbs only a little of the energy of the 3650 line, which itself contains 25 percent of the energy contained in the three lines. The hypothesis that light received by benzoin alone is active may be tested by isolating this line and comparing the rate of subsequent reaction with that when all three lines are present. This can be done with the aid of Corning filter No. 5874, which passes 50 percent of line 3650 Å, but blocks completely lines 4358 Å and 4045 Å. Since zinc porphin also absorbs 3650 Å light to a considerable extent, we should expect to find about 50 percent x 25 percent or 12-1/2 percent as much reaction with the filter imposed as when not, if light absorbed by the porphin in all three bands is active. If benzoin light alone is active, we should of course expect to find 50 percent as much reaction. When this was done during the course of one of the rate runs, the actual amount found was 14 percent. As this was in agreement with previous qualitative work showing the 3650 Å line to be not especially active, it was duly concluded that light of the wave length of the Soret and ultraviolet bands of zinc porphin was active, and calculations were made on that basis.

The runs wherein benzoin concentration was varied were continued. They showed a rough but definite linear dependence of the reaction rate on the concentration of benzoin, over a fortyfold range of benzoin concentration. The porphin concentration could not be varied much, because the reaction had to be followed by taking spectra of the porphin, but variation over about a threefold range was tried. The results were erratic; it was impossible to choose between a zero-order and a first-order dependence on porphin concentration. The feeling that something was wrong led to further experiments on dependence of reaction on wave length, carried out with the aid of some newly acquired filters.

Reduction was followed, using alternately filters No. 9700 and No. 3850. Filter No. 9700 passes 90 percent of the light in lines 4358 and 4045 Å, 80 percent of light in line 3650 Å. Filter No. 3850 passes 86 percent of line 4358 Å, 84 percent of line 4045 Å, and 32 percent of line 3650 Å. The results are shown

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[*] The apparent slight rise in porphin optical density during illumination with yellow light should probably be attributed to changes in the degradative oxidation products also present. Such changes are hard to take into account in finding D_p.
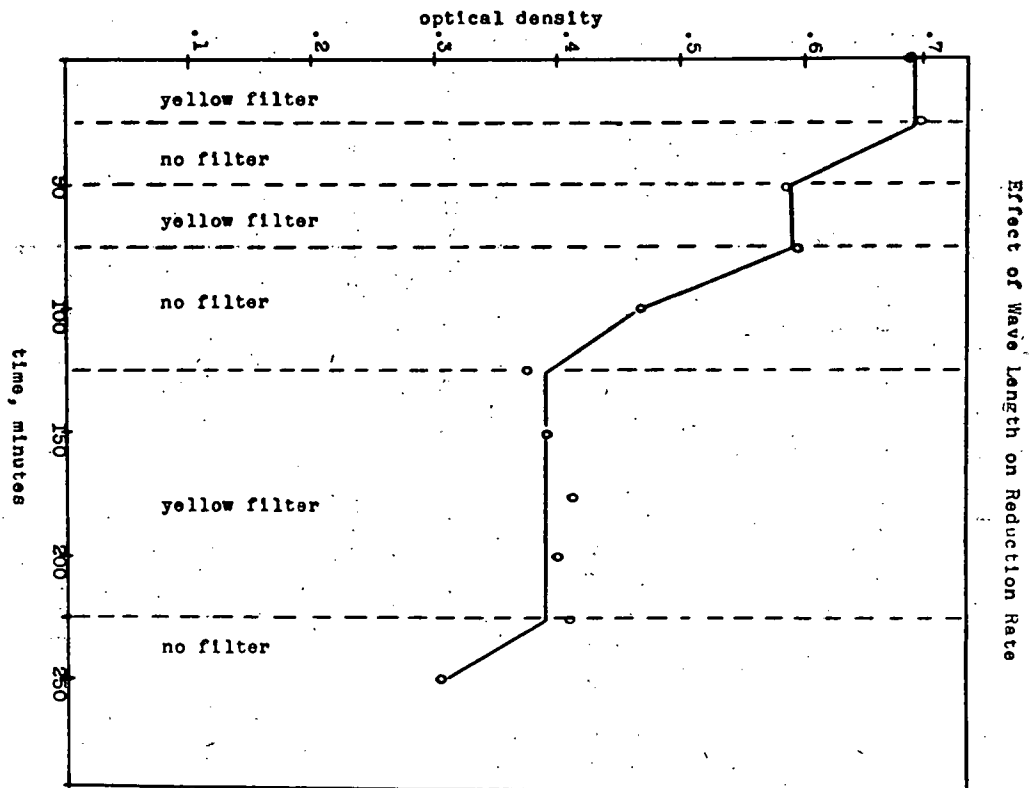
Fig. 20

Effect of Wave Length on Reduction Rate

in Table IV; the ratio of reduction with filter No. 9700 to that with No. 3850
is 3:1, which is the ratio one would expect if light absorbed by the benzoin,
3650Å, is alone active.

A rate run was made, this time comparing filters No. 9700 and No. 9872,
which passes 60 percent of line 4358Å, 45 percent of line 4045 Å and only about
three percent of line 3650Å. The amount of reduction obtained when filter No.
9782 was imposed was less than four percent of that when No. 9700 was used.
It was now apparent that light absorbed by the benzoin was responsible for the
reaction, but this conclusion could not be consistent with earlier results unless:

(a) Reaction rate is proportional to a power higher than first of the light
    intensity, or

(b) Light must be absorbed by the porphin also.

Two types of experiments were now undertaken. Three experiments
were conducted, comparing rates of reduction at normal and diminished light
intensities. Light was diminished, for these experiments, by factors of 1/2,
1/3, and 1/5 by means of a card, from which sectors had been cut, placed over
the aperture of the irradiation box. Resumés of these three runs appear in Tables
IV and V. Apparent is a dependence on light intensity higher than first power,
well beyond experimental error. The power dependence approaches 3/2; but
it could of course also be the sum of the two terms, one containing light
intensity squared, the other the first power.

The other type of experiment was designed specifically to test whether
or not light absorbed by the porphin augmented the reaction rate. The left
half of the aperture of the irradiation box was covered by filter No. 5970, which
passes almost exclusively light absorbed by the benzoin, and the right half of
the aperture was covered by filter No. 3385, which passes no light absorbed
by the benzoin, but only light of the long-wave-band system of zinc porphin,
light that has been shown by several experiments to produce no reaction what-
soever when it is the sole excitation. The tube is now illuminated with a card
alternately covering and not covering filter No. 3385. If light absorbed by
the porphin plays no role in the reduction, then the rate should be the same
whether or not a card covers filter No. 3385. What is actually found, as the
table below shows, is a considerable augmentation of the reaction rate when
the supposedly "dead" light of wave length greater than 490 mμ is allowed to
strike the tube.

TABLE IV
Effects of Filters No. 9700 and No. 3850 on Reduction of Porphin

Interval	Duration min.	Filter	Reduction rate moles/min.	Ratio of rates, moles/min.	$\dfrac{\text{with } 9700}{\text{with } 3850}$
I	10	9700	5.4×10^{-7}		
II	10	3850	2.0 "	2.7	
III	10	9700	5.3 "		
IV	10	3850	1.0 "	4.5	
V	10	9700	3.7 "		
VI	10	3850	1.8 "	1.8	
VII	10	9700	2.7 "		
				av.: 3.0	

TABLE V
Effects of Filters No. 9700 and 9782 on Reduction Rate

Interval	Duration mins.	Filter	Op. Dens. change	Red. rate, moles/ min.	Ratio of rates
I	10	9782	-.023	-------	
II	10	9700	+.074	3.3×10^{-7}	
III	60	9782	+.015	0.11×10^{-7}	*28:1
IV	16	9700	+.104	2.9×10^{-7}	

Summarizing, the reaction rate is evidently proportional to the amount of light received by the benzoin, but light received by porphin augments the rate. Aside from the effect of porphin on light absorption, the dependence on porphin concentration is still unknown.

The concurrent reduction of zinc chlorin appears to have the same light requirement as the reduction of porphin, judging from the behavior of the chlorin band, which changes in optical density only when the porphin band changes. Whether light received by chlorin augments the rate of its reduction by benzoin remains uncertain. The same may be said of the reduction of zinc tetrahydroporphin. This matter would require further study, using pure preparations of these compounds.

The cause of inhibitions reported for the reduction is now clear, except in the case of strong bases like piperidine. The inhibitors benzil, quinoline, and Apiezon N grease all absorb in the near ultraviolet and interfere with absorption of light by benzoin.

Reduction of Data and Tabulation of Results

Let us now turn our attention to the procedure for calculating quantum yields. From the spectra obtained at intervals, optical densities are gathered, and from these the concentration of zinc porphin, and of anything else in the solution we desire, must be determined.

When porphin first begins to be reduced, the band at 618 mμ, characteristic of zinc chlorin, rises and reaches an approximate steady-state optical density of about 0.2. Following the chlorin band emerges the band at 602 mμ characteristic of zinc tetrahydroporphin, from the shoulder of a small porphin band at 587 mμ. This 602 band increases in strength during the reaction, although the increase rate slows as the reaction proceeds. Tetrahydroporphin is certainly being reduced as the reaction continues, but none of its reduction products have bands that can be distinguished. All this time the band with peak 550 which characterizes zinc porphin (all these runs are in benzene solution), is decreasing. The presence of residual traces of oxygen in the tube becomes apparent through arising, at the beginning of the reaction, of a small sharp peak at 463 mμ, of optical density varying between 0.03 and 0.2, which decays slowly during the course of the run. Since the peak of the final oxidation product of porphin is at 530 mμ, a slow rise in this part of the spectrum is observed from that cause. Furthermore, the optical density of the whole spectrum rises slowly throughout the reaction,

TABLE VI

Dependence of Reduction Rate on Light Intensity

Interval	Duration mins.	Light Intensity	Op. dens. change	Red. Rate moles/l./min.	Ratio, rates high/low
			FIRST EXPERIMENT		
I	10	high	.075	3.4×10^{-7}	
II	10	low	.031	1.4 "	2.9
III	15	high	.155	.46 "	
IV	15	low	.039	1.2 "	
V	15	low	.056	1.7 "	2.9
VI	15	high	.129	3.9 "	

Ratio of light intensities, high/low, was 2.15

Av. ratio of reduction rates, high/low, 2.9

Av. ratio of quantum yields, high/low, 1.35

Interval	Duration mins.	Light Intensity	Op. dens. change	Red. Rate moles/l./min.	Ratio, rates high/low
			SECOND EXPERIMENT		
I	5	low	.020	1.8×10^{-7}	
II	5	high	.136	12.2 "	6.3
III	10	low	.047	2.1 "	
IV	10	low	.044	2.0 "	
V	5	high	.103	9.3 "	5.6
VI	10	low	.028	1.3 "	
VII	10	low	.030	1.3 "	
VIII	10	high	.131	5.9 "	4.9
IX	30	low	.066	1.0 "	

Ratio of light intensities, high/low, was 3.3

Av. ratio of reduction rates, high/low, 5.6

Av. ratio of quantum yield, high/low, 1.7

Interval	Duration mins.	Light Intensity	Op. dens. change	Red. Rate moles/l./min.	Ratio, rates high/low
			THIRD EXPERIMENT		
I	5	high	.129	12.7×10^{-7}	
II	25	low	.053	1.04 "	11.0
III	5	high	.104	10.2 "	
IV	25	low	.061	1.20 "	
V	5	high	.065	6.4 "	6.3
VI	25	low	.043	0.82 "	
VII	10	high	.112	5.5 "	7.4
VIII	50	low	.066	0.75 "	

Ratio of light intensities, high/low, was 5.1

Av. ratio of reduction rates, high/low, 8.2

Av. ratio of quantum yields, high/low, 1.6

TABLE VII

Augmentation of Reduction Rate
by Yellow Light

Interval	Duration mins.	Filters	Red. Rate moles/l./min.	Rate Ratio with No. 3385 without
I	15	5970 + 3385	3.02×10^{-7}	
II	15	5970	0.90 "	1.98
III	15	3385	0.39 "	
IV	15	5970 + 3385	2.07 "	
V	15	5970	0.90 "	2.20
VI	15	5970 + 3385	1.89 "	
VII	15	5970	0.96 "	1.76
VIII	15	3385	-0.03 "	
IX	15	5970 + 3385	1.38 "	
X	15	5970	0.66 "	1.98
XI	15	5970 + 3385	1.23 "	
				Av: 1.98

owing to the presence of additional reduction and degradative oxidation products of porphin, benzil, and light scattering which is sometimes introduced when a little of the silicone grease washes into the solution.

The intent of the calculation is this: To find the optical density of zinc porphin as a function of time, and by extrapolating to zero time and taking the slope, to find the initial rate of decay of zinc porphin. The concentration change may be calculated from the change in optical density.

The spectrum is taken from 650 mμ, which is just beyond the region where porphin or any of its reduction products absorb, to 450 mμ, which is at the foot of the Soret band. With the aid of optical densities at 550, 520, and 602 mμ, the optical density of the porphin band at 550 mμ will be determined. Let D_{650}, etc. represent the optical density read off the spatial tracing at 650 mμ, etc. Let also D_p represent the optical density of the porphin band at 550, if only porphin were present D_c the chlorin band at 618 if only chlorin were present, D_t the optical density of tetrahydroporphin at 602 if only that were present. These are proportional to the true concentrations of the three substances, and these we wish to calculate.

We have mentioned that there is a general absorption in the whole spectral range once the reaction has started. To the red side of 550 mμ, the amount of this may be estimated by D_{650}, where none of the porphyrins themselves absorb. Hence densities of the bands at 602 and 618 mμ are corrected for this general absorption by subtracting D_{650}. Let

$$D'_{602} = D_{602} - D_{650}$$
$$D'_{618} = D_{618} - D_{650}$$

The primed D's represent optical densities due to porphin and its reduction products only.

General absorption in the vicinity of the main porphin band is removed by recalling that the ratio, in pure porphin solution, of D_{550} to D_{520} is 7.4. If we have in our solution along with porphin something that absorbs an unknown but identical amount D_x at 550 and 520 mμ, the observed ratio of these optical densities will be:

$$\frac{D_{550}}{D_{520}} = \frac{D_p + D_x}{\frac{1}{7.4} D_p + D_x}$$

Solving, $D_x = \dfrac{D_{520} - \dfrac{D_{550}}{7.4}}{\dfrac{D_{550}}{D_p} - \dfrac{D_{520}}{D_p}}$

D_p is unknown, but $\dfrac{D_{550} - D_{520}}{D_p} = \dfrac{1 - 1/7.4}{1}$

so that $D_x = \dfrac{7.4\, D_{520} - D_{550}}{6.4}$

We form the first approximation to D_p by setting

$$D'_{550} = D_{550} - D_x = \frac{7.4}{6.4}(D_{550} - D_{520}).$$

This approximation accounts for substances absorbing equally at 550 and 520 mμ.

Now a glance at the spectrum will show that zinc chlorin has almost the same extinction coefficient at 550 mμ as it has at 520 mμ. Hence the correction above has included a subtraction of the optical density due to chlorin at 550 mμ. As far as the accuracy of our work permits, this correction subtracts out absorption due to oxidative degradation products, reduction products beyond the tetrahydro, and light scattering, if there is any. To obtain D_p, it only remains to subtract out absorption due to zinc tetrahydroporphin.

Now D'_{602} does not represent absorption by tetrahydroporphin alone; both chlorin and porphin absorb at that wave length. The extinction coefficient of chlorin at 602 mμ is not large, and since chlorin is present in these solutions in quite small concentration, its absorption at 602 may, in our approximation, be neglected. Porphin does absorb appreciably; in practice its effect is accounted for by taking the values at zero time $D_{550,\ init}$ and $D_{602,\ init}$ and forming

$$D_t = D'_{602} - \frac{D_{602,\ init}}{D_{550,\ init}} \times D'_{550}.$$

Then, as the spectrum of zinc tetrahydroporphin shows,

$$D_p = D'_{550} - .07 \times D_t.$$

This is the value for the optical density of zinc porphin, which is tabulated or plotted as a function of time.

The next step in the calculation of quantum yield is to obtain the amount of light absorbed by the benzoin. The total amount of light passing through the tube is measured by the bolometer, in watts. From the calibration of the sunlamp, it is known that 7.6 percent of this light is in line 3650 Å, and no measurable amount

is emitted (or passed by the optical system) further in the ultraviolet. For compatibility of units, the light flux is divided by the volume of solution. Let F be the total flux, in watts. Then $0.076\ F/v$ is the number of watts per liter in line 3650 $\overset{o}{A}$ passing into the reaction tube.

The Beer-Lambert Law for change of intensity of light passing through a solution is

$$dF = -Fecdl$$

where F is the intensity, e is extinction coefficient, c is concentration, 1 the path length. By integration and change of base of the exponents, it is seen that the amount of light absorbed in the solution after path length 1 is:

$$F_{abs} = F_o (1 - 10^{-ecl}) = F_o (1 - 10^{-D})$$

where D is the optical density.

Therefore the amount of light absorbed by the solution in the tube in watts per liter at 3650 $\overset{o}{A}$ is:

$$F_{abs} = 0.076\ F/v\ (1 - 10^{-D365})$$

Not all this light is absorbed by benzoin. The ratio of the amounts absorbed by porphin and benzoin is the ratio of the optical densities of the two compounds. Or, using subscripts p for porphyrin, b for benzoin, e for extinction coefficient, and c for concentration,

$$\frac{\text{light abs. by benzoin}}{\text{total light absorbed}} = \frac{e_b c_b}{e_b c_b + e_p c_p}$$

The extinction coefficient of benzoin at 3650 $\overset{o}{A}$ is 8.7; that of zinc porphin is 7800. These numbers may be substituted into our expressions, and, using P and B for porphin and benzoin concentrations, we obtain, for the total light absorbed by the benzoin, in watts per liter,

$$0.076\ F/v\ \frac{8.7\ B}{8.7\ B + 7800\ P}\left(1 - 10^{-0.96\ (8.7\ B + 7800\ P)}\right)$$

We must now convert this number to quanta per liter per second. One watt is 10^7 ergs per second. The energy, in ergs, of a quantum of light of wave length λ is given by Planck's Law: $E = \frac{hc}{\lambda}$, where h is Planck's constant and c is the velocity of light. The number of quanta, then, is the number of ergs divided by the energy per quantum in ergs, and this divided by Avogadro's number gives the number of einsteins, or "moles", of light absorbed by the benzoin per second.

$$\text{Einsteins/sec} = \text{watts} \times 10^7\ \lambda/hcN$$

The numerical constants:

$$h: 6.6 \times 10^{-27} \text{ erg sec.}$$
$$c: 3.0 \times 10^{10} \text{ cm/sec}$$
$$\lambda: 3.65 \times 10^{-5} \text{ cm}$$
$$N: 6.02 \times 10^{23} \text{ molecules}$$

Performing the appropriate arithmetic, including multiplication by 0.076, we find the light absorbed by the benzoin, in einsteins per liter per second, is

$$F_B = 2.33 \times 10^{-7} \, F \, \frac{8.7 \, B}{8.7 \, B + 7800 \, P} \left(1 - 10^{-0.96 \, (8.7B + 7800 \, P)}\right)$$

The calculation of the number of einsteins of light received by the porphin is a little more tedious. Account must be taken of the distribution of emitted light among the five principal mercury lines, the absorption by porphin of each of these lines, and the number of quanta per erg in each of the several lines. Let F be the total flux in watts, the subscript i denote a mercury line, and r denote the fraction of the total energy which is in a line, so that $F_i = r_i F$. The amount of energy absorbed by porphin solution of concentration P from that line is then

$$F r_i \left(1 - 10^{-0.96 e_i P}\right)$$

and the total amount of energy absorbed by the porphin is the sum over all i of this expression. The power in each line is converted, as before, into einsteins per second, for the case of benzoin, by multiplying by $\frac{10^7 \lambda_i}{hcN}$. The number of einsteins per liter per second absorbed by the porphin is found by summing and dividing by the volume

$$\frac{F_p}{v} = \frac{10^7 F}{v \, hcN} \, \Sigma_i \lambda_i r_i \, \left(1 - 10^{-0.96 e_i P}\right)$$

The sum appearing in this expression has been calculated for several values of porphin concentration, and a graph drawn, plotting it as a function of porphin concentration. The r's and λ's may be obtained from Table II; the appropriate extinction coefficients may be read from the spectrum of porphin, Fig. 3. Multiplying out the numerical factors, a final expression for the total number of einsteins per second per liter is:

$$\frac{F_p}{v} = 0.084 \, \frac{F}{v} \, \Sigma_i r_i \lambda_i \, \left(1 - 10^{-0.96 e_i P}\right)$$

Fig. 21

Fraction of

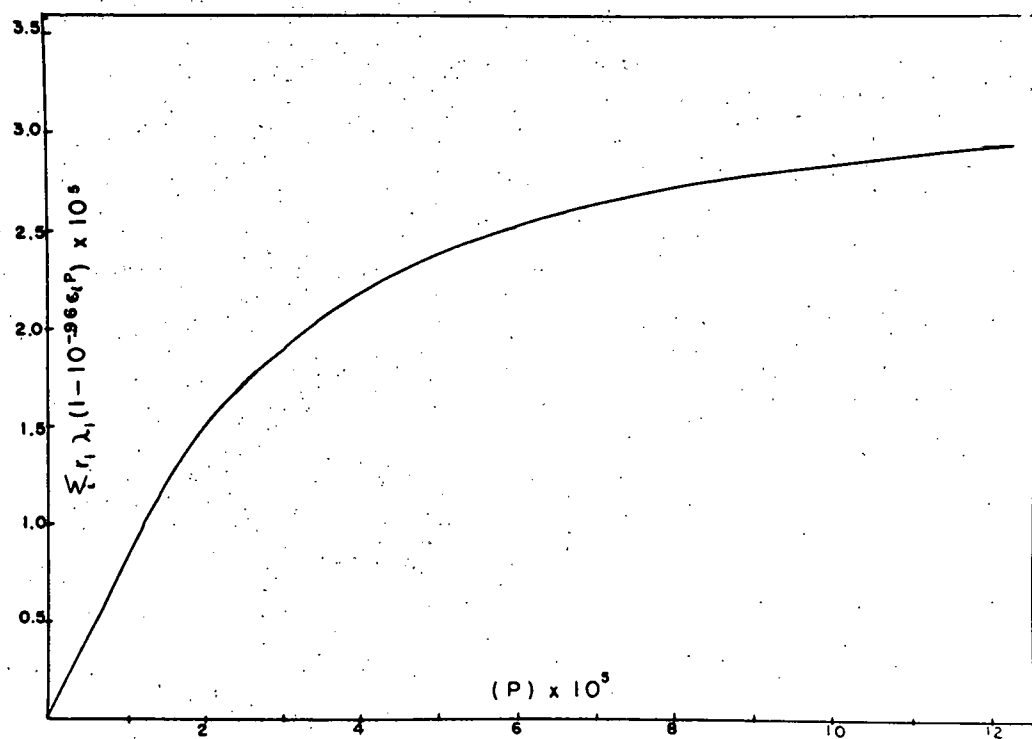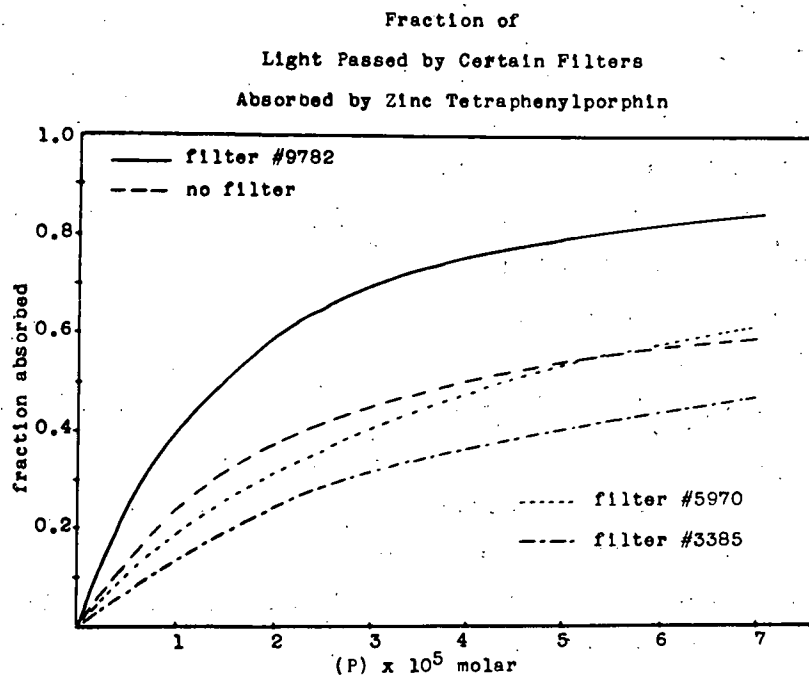Light Passed by Certain Filters

Absorbed by Zinc Tetraphenylporphin

Light Source: G. E. Reflector Sunlamp

Path Length through Porphin Solution: 1 cm.

Fig. 22

The tabulation of the results is shown in Table VIII. In it are listed the concentrations of zinc porphin and of benzoin, the flux in watts per liter through the tube, the initial rate of reduction of zinc porphin, the light absorbed by benzoin in einsteins per liter per second, the light absorbed by porphin in those units, and the quantum yield based on light absorbed by benzoin. The rate of reduction of porphin, the moles per liter per second, is calculated from the change in optical density, since

$$D = ePI, \quad \frac{dP}{dt} = \frac{1}{eI} \frac{dD}{dt} = \frac{1}{0.96 \times 22,200} \frac{dD}{dt}$$

for the extinction coefficient of zinc porphin at 550 mμ is 22,200. The quantum yield, based on light absorbed by benzoin, is found by dividing the reduction rate by the light absorbed by the benzoin. This tabulation includes also runs in which the intensity was varied, entered twice. One of the experiments in which the aperture was covered by two filters is also included.

It will be seen that most of the quantum yields gather around a value of 0.05, regardless of the benzoin or porphin concentrations, except those in which the light intensity is reduced. There is evidently no further dependence on benzoin concentration, since that concentration varies over a fortyfold range. Similarly, no particular dependence on porphin concentration can be pinned down. Because of the impossibility of initial rate measurements, and the inaccuracy of any other, no attempt was made to study the rate of reduction of chlorin. It is evident, though, on inspection of the spectra, that chlorin is reduced about ten times as fast as porphin.

Since it is known that light absorbed by the porphin augments the quantum yield, a plot is made of quantum yield based on benzoin against light absorbed by porphin. The points are scattered loosely with an upward trend from a nonzero intercept. If the best straight line is drawn through these points,[*] we find a rate law of the form:

$$\frac{dP}{dt} = kF_b + k'F_bF_p ,$$

so that the straight line through the points will be:

$$\frac{1}{F_b} \frac{dP}{dt} = k + k'F_p$$

No further dependence on any of the variables can be ascertained by inspection of the points. This is, therefore, the best rate law that can be found experimentally.

Only a theoretical treatment of this reaction will enable us to refine this rate law; we shall find, on such refinement, an agreement between experiment and theory commensurate with the accuracy of the experimental data.

[*] Found by a least-squares analysis of the data. Cf. Margenau and Murphy, Mathematics of Physics and Chemistry, Van Nostrand, 1943, p. 500.

Reduction of Zinc Tetraphenylporphin by Benzoin in Benzene:
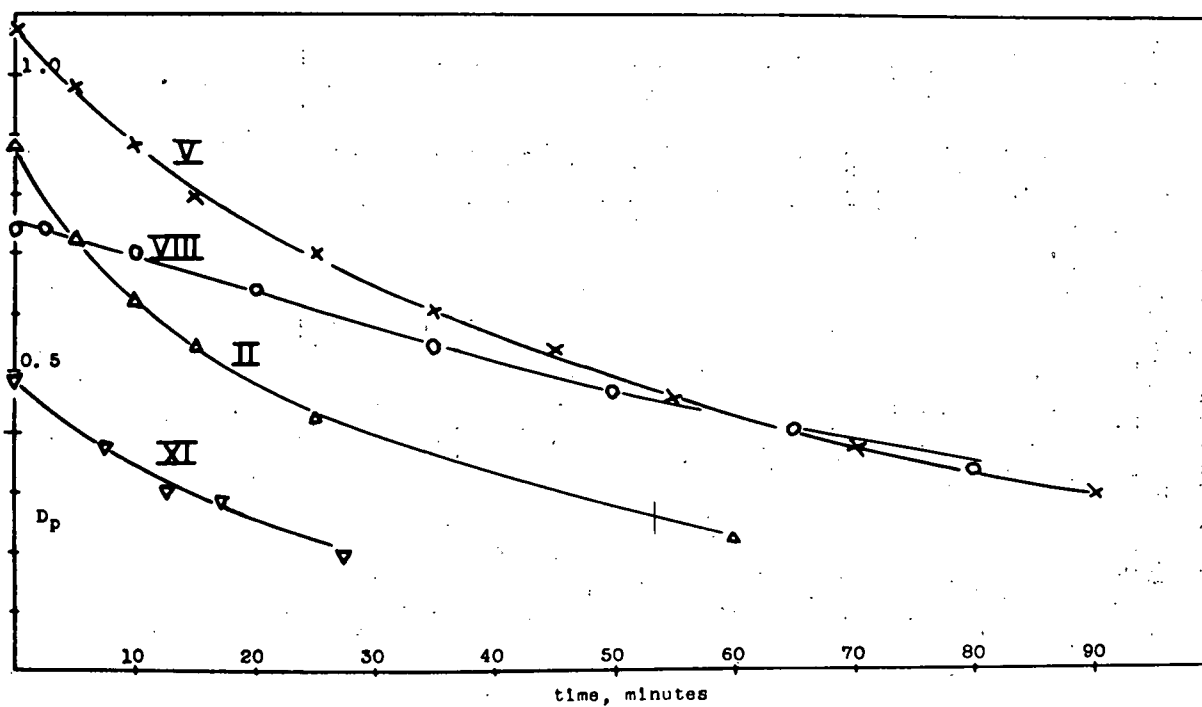
Followed by Fall of Porphin Band

Fig. 23

Summary of Results of Rate Runs on Reduction of Zinc Porphin by Benzoin

| Run. No.	Porphin conc, molar	Benzoin conc, molar	F, watts/liter	F_b, einsteins/(liter·sec)	F_p, einsteins/(liter·sec)	Initial rate, moles/sec	Quantum yield
I	5.1×10^{-5}	3.3×10^{-3}	6.9	6.7×10^{-8}	1.40×10^{-5}	3.7×10^{-9}	0.055
II	4.1 "	32.0 "	6.7	55.0 "	1.24 "	21. "	0.038
III	5.74 "	0.75 "	8.8	1.9 "	1.85 "	1.03 "	0.054
IV	4.7 "	18.2 "	8.8	43.0 "	1.73 "	17.1 "	0.040
V	5.1 "	9.6 "	8.1	21.0 "	1.64 "	14.2 "	0.068
VI	5.4 "	6.2 "	8.0	13.7 "	1.65 "	7.6 "	0.055
VII	5.75 "	1.9 "	6.9	3.6 "	1.46 "	2.0 "	0.056
VIII	6.94 "	5.3 "	7.0	9.4 "	1.56 "	4.8 "	0.053
IX	6.6 "	6.9 "	7.2	13.0 "	1.59 "	6.8 "	0.052
X	2.4 "	7.9 "	7.9	21.5 "	1.12 "	12.4 "	0.058
XI	2.25 "	7.9 "	6.8	19.0 "	0.93 "	11.1 "	0.058
XII	5.55 "	9.2 "	8.1	18.0 "	1.68 "	7.8 "	0.043
XIII	5.6 "	26.1 "	6.8	42.0 "	1.42 "	21. "	0.050
	5.6 "	26.1 "	2.05	12.6 "	0.43 "	3.8 "	0.030
XIV	5.1 "	16.5 "	----	12.9 "	0.04 "	1.76 "	0.014
	5.1 "	16.5 "	----	12.9 "	0.38 "	5.2 "	0.026
XV	4.85 "	18.0 "	7.8	37.5 "	1.55 "	17.3 "	0.046
	4.85 "	18.0 "	1.55	7.5 "	0.31 "	2.1 "	0.027
XVI	11.4 "	15.0 "	7.2	20.0 "	1.78 "	9.4 "	0.047
XVII	2.44 "	1.30 "	6.7	4.5 "	0.96 "	2.07 "	0.046
XVIII	2.63 "	7.9 "	2.75	7.4 "	0.41 "	3.3 "	0.045
XIX	5.0 "	16.1 "	2.9	12.3 "	0.58 "	3.3 "	0.027
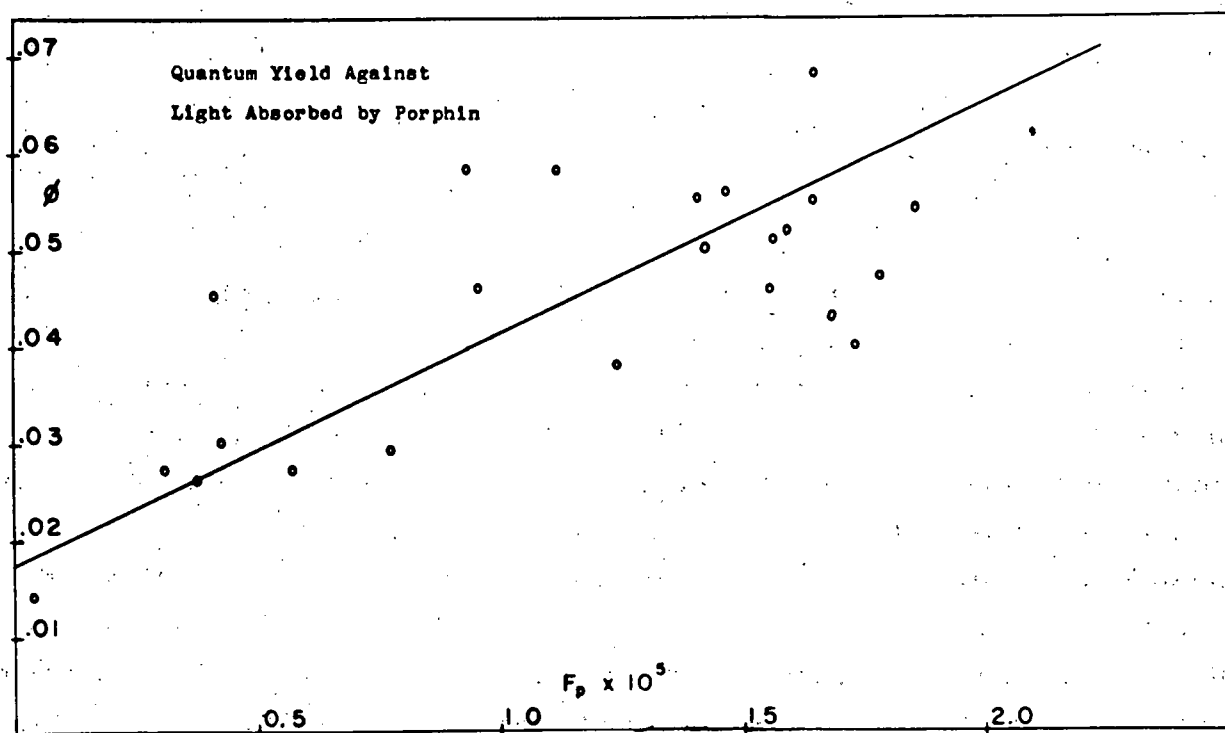
Fig. 24

Derivation of a Rate Law: Comparison with Experiment

Let us now turn to the central problem of this thesis, the determination of a mechanism for the reaction. Since the reaction is photochemical, it will be well to review in some detail what we know of the photochemistry of benzoin and of porphin, which, with the aid of kinetic theory and a few judicious guesses will enable us to postulate a mechanism consistent with the facts. Let us begin by studying the interactions of zinc tetraphenylporphin with light.

The accompanying diagrams illustrate the relationships between the known electronic states of porphin, and show the wave length of the light involved in the transitions between them. The absorption spectrum of zinc porphin shows five band systems, as has been previously mentioned, two of which are in the visible part of the spectrum, three in the ultraviolet ; corresponding to these are the five singlet excited states of the diagram, labeled S_1, etc., to which transitions from the singlet ground state are allowed. The first excited state, S_1, may be called the fluorescent state of zinc tetraphenylporphin, for a solution of porphin excited to this state exhibits a strong red fluorescence with intensity maximum at 6500 Å, indicated by a downward arrow on the diagram.[9] The fact that excitation with light absorbed by the porphin in any of its bands produces red fluorescence and no other serves to illustrate the rule that molecules raised to the higher excited states are degraded almost immediately to the lowest excited state, in which state they may either fluoresce, or be degraded to the ground state thermally or by influence of electromagnetic fields of the solvent molecules (quenching).

Since the absorption and fluorescent spectra of zinc porphin do not overlap, this molecule is apparently of the type in which the vibrational state must change whenever the electronic state does. Since most of the molecules in the ground electronic state are also in the lowest vibrational level, they may be excited only to higher vibrational levels of the first excited electronic state, S_1. From these the molecule is promptly thermally degraded to the lowest vibrational level, from which, by fluorescence, the molecule passes to a higher vibrational level of the ground electronic state. This situation, which is illustrated in the more detailed diagram, is the generally accepted explanation of why fluorescence lies to the

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*   We are indebted to Dr. D. S. McClure for his guidance in this discussion.

Energy Level Diagram
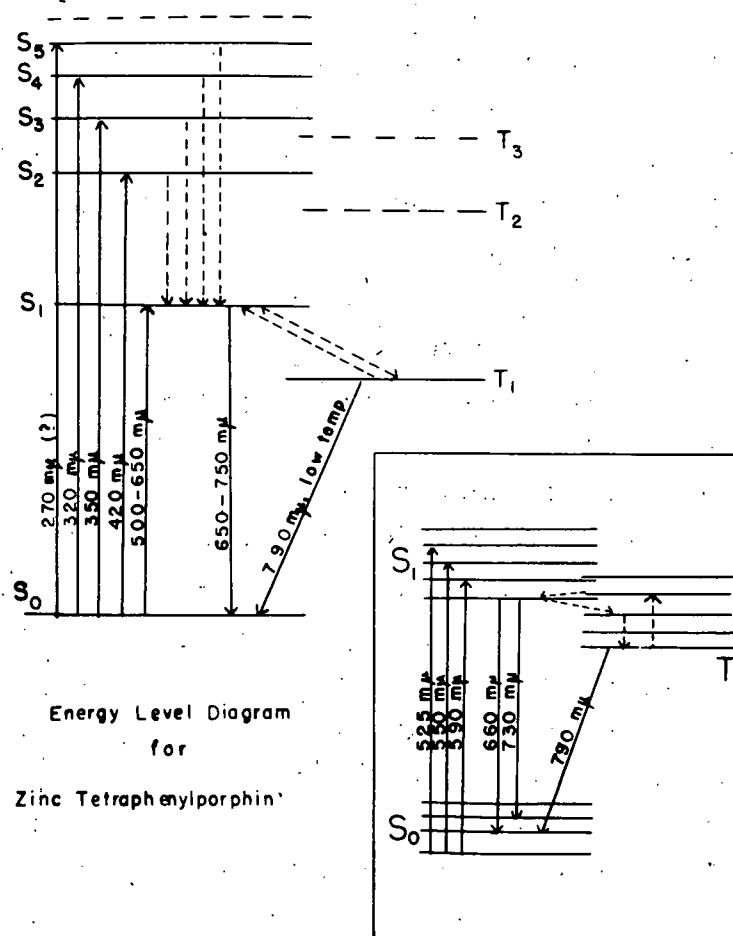for
Zinc Tetraphenylporphin

Fig. 25

long-wave side of the corresponding absorption band, and also explains a rough mirror-image relationship between fluorescence and absorption spectra found in many compounds.[17, 42]

Zinc tetraphenylporphin possesses a phosphorescent state, the first excited triplet state. Radiative transitions between this state and singlet states are forbidden, not by symmetry, but by difference of electronic spin. However, when a triplet state and a singlet state have nearly the same energy, and their vibrational levels overlap, the multiplicity restrictions are such that nonradiative transitions may occur rather frequently between the lowest vibrational level of the singlet excited state and the upper vibrational levels of the triplet excited state, as shown on the diagrams. At low temperatures, the "forbidden" transition between the triplet state and the ground state has been observed as phosphorescence of wave length 7900 Å.[9] Phosphorescence, of lifetime approaching a hundredth of a second, has been observed at room temperature in anaerobic hydrocarbon oil solutions, but not in anaerobic benzene solution, although here it might have been quenched by traces of oxygen still present. No spectrum could be taken, but this emission is probably of the same light as the fluorescence, and arises when molecules in the triplet state are excited from the lowest to an upper vibrational level by collisions, then pass over to a vibrational level of the singlet state, from which they fluoresce. This can happen when the temperature is such that the probability that a molecule will be knocked up to a higher vibrational level is greater than the probability that it will decay directly to the ground state.

The energy-level system for benzoin is qualitatively the same as that for porphin. Absorption to the first singlet excited state begins at about 3700 Å;[*] the fluorescence, weaker than that of porphin, is blue. Rather little seems to be reported about the phosphorescence of benzoin; Kirchof reports yellowish phosphorescence of the crystals,[22] and we have detected phosphorescence in hydrocarbon oil solution, of lifetime around three thousandths of a second. We have already mentioned that benzoin, acetophenone, and other compounds behave similarly toward porphin and oxygen; a consistent explanation of this involves assumption of a triplet state attainable by each of these compounds. Let us, then, take as granted that under the conditions of our reaction, there are molecules of benzoin in a relatively long-lived triplet state when our solutions are irradiated by light absorbed by benzoin.

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[*] For the spectrum of benzoin, not necessary for this work, see American Petroleum Institute Research Project 44, Catalogue of Ultraviolet Spectral Data, Carnegie Institute of Technology, No. 348.

Aside from the reactions which form topics for this thesis, the only photo-chemical reactions of this series of porphyrins are the oxidations, the results of which are summarized in the introduction. Very little is known about the photochemistry of benzoin. There is one report that benzoin, dissolved in concentrated acetic acid, polymerizes during exposure to sunlight for five months.[33]

Any mechanism we may postulate for this reaction must take into account three salient facts: There is no sign whatever of any complexing between the porphin and benzoin, for the spectrum of porphin is the same whether benzoin is present in the solution or not; light absorbed by the benzoin is both necessary and sufficient for the reaction, but light absorbed by the porphin may triple the quantum yield; the quantum yield is rather high, as much as 0.06 at high light intensities. The first of these facts means that the rate of the reaction will be bounded above by the number of collisions between benzoin and porphin molecules in proper states; this consequence, together with the latter two facts, will put a restriction on the type of excited states involved in the reaction.

First of all, let us compare the numbers of molecules we may expect to find in the singlet and triplet excited states of benzoin or porphin, when solutions are irradiated under our experimental conditions. Let us assume that a solution containing only zinc porphin is receiving I_p einsteins per liter per second of light, and that excited porphin decays with a lifetime τ.* Let us now designate the concentration of porphin excited into the first singlet excited state by P'; then during a time interval dt, $dP' = I_p dt - P'/\tau dt$. At steady state, $dP' = 0$, or $P' = \tau I_p$. For the fluorescent state of porphin, an estimate of the lifetime is $\tau = 10^{-8}$ secs. Since, under the conditions of the reaction, I_p is around 1.5×10^{-5} einsteins per liter per second, P' is approximately 1.5×10^{-13} molar.

Benzoin, having a weak first absorption band, may have a fluorescence lifetime as long as 10^{-6} secs. I_b is about 20×10^{-8}, and hence, at fairly high concentrations B' may be about 2×10^{-13}.

The population of molecules in the excited triplet state is subject to two considerable uncertainties. First, an unknown fraction a of the molecules excited to the singlet state makes the radiationless transition to the triplet state. Several reactions are known that proceed through such a transition with quantum

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* The lifetime is defined as follows: If at some time after light is turned off, there are N excited molecules, the rate of decay is $\dfrac{dN}{dt} = \dfrac{N}{\tau}$. Integrating, $N = N_0 e^{-\frac{t}{\tau}}$, where $N = N_0$ at $t = 0$. Hence, when $t = \tau$, $N/N_0 = 1/e = 0.368$.

yield approaching one. The fraction a may be as high as $1/2$ for our molecules; the quantum yield tells us it is certainly greater than $1/20$. The other uncertainty is the lifetime, which varies considerably with the solvent and the termperature. For this demonstration, we shall take $a = 0.1$ and $\tau = 10^{-3}$, both reasonable values.

To find steady-state concentrations of molecules in the triplet state we equate rates of production and decay: for porphin, $aF_b = P''/\tau$, or $P'' = \tau aF_b = 1.5 \times 10^{-9}$ molar; for benzoin, $B'' = \tau aF_b = 2 \times 10^{-11}$ molar.

It is instructive to compare the average time elapsing between collisions of a benzoin molecule with porphin molecules with its fluorescent and phosphorescent lifetimes. To do this, we must assume that the solution behaves like a perfect gas -- a rather improbable supposition, but we hope that results of the right order of magnitude may be obtained thereby. From kinetic theory, then, the average time between collisions is:[38]

$$t = \frac{1}{2\sigma_{12}^2 \, n_2 \sqrt{\frac{2\pi RT}{M}}}$$

where σ_{12} is the average diameter of benzoin and porphin, n_2 is the concentration of porphin in molecules per cc. and M is the reduced molecular weight,

$$M = \frac{m_b m_p}{m_b + m_p} = 162,$$ where m_b and m_p are the molecular weights of benzoin and zinc porphin, respectively. Now σ_{12} is a rather uncertain number; Dorough, in his thesis, uses the value 4×10^{-8} cm., and we shall continue to use this value. $R = 8.3 \times 10^7$ ergs/mole/degree, and $T = 300^\circ K$. If we substitute the numerical factors, we obtain:

$$t = \frac{1}{10^{-10} \, n_2}$$

If we take the concentration of zinc porphyrin as 5×10^{-5} molar, or

$\dfrac{5 \times 10^{-5} \times 6 \times 10^{23}}{1000}$ molecules per cc., then the time between collisions of benzoin molecules with excited porphin molecules is about 3×10^{-7} secs. Similarly if we take the concentration of porphin molecules excited to triplet state to be 1.5×10^{-9} molar, the average time between collisions of benzoin with excited porphin is found to be 1.1×10^{-2} secs. It should perhaps be pointed out that these computations in no way depend upon the electronic state of the benzoin.

Now it must be recalled that excited porphin molecules account for at least 2/3 of the reaction at higher light intensities, and with high quantum yield. The lifetime for benzoin in its singlet excited state may be as high as 10^{-6} secs., but still only one molecule in ten thousand would be likely to collide with a porphin molecule in its triplet excited state. Benzoin in its triplet excited state, with decay parameter probably greater than 10^{-3} secs., has a much better chance of colliding with excited porphin, so it must be in this triplet state that benzoin reacts. In no other way can the quantum yield actually found be approached.

We are now ready to derive an expression for the rate law. We take as given that benzoin in the triplet excited state may reduce zinc porphin upon collision with the latter in its ground state or in its triplet excited state. Again we recall the outstanding datum of this reaction: Excited porphin accounts for two-thirds of the reaction, even though there is ten thousand times as much unexcited porphin present. Corollary to this, an excited benzoin molecule must collide with thousands of unexcited porphin molecules before reaching (and reducing!) an excited porphin molecule. We therefore assert that most collisions between benzoin and ground-state porphin result in neither reduction nor deactivation, but that, on the average, only one collision in n collisions results in either reduction or deactivation. Since, at a given level of light absorbed by the porphin, the quantum yield appears to be independent of porphin concentration, the number n must be small enough that an excited benzoin molecule has a pretty good chance of reacting with ground-state porphin, provided it does not react with excited porphin first. On the other hand, n must be large enough that an excited benzoin molecule has a better chance of reacting with an excited porphin molecule than with an unexcited porphin molecule, at high light intensities. The number n should be at the very least 100, and 1000 would be a more likely guess.

We shall restate this argument in terms of the activated complex theory of reactions. The activated complex is defined here as a union of a benzoin and a porphin molecule, arrived at by collision, and such that upon dissolution the benzoin either has reduced the porphin, or has suffered deactivation to the ground state, induced by the electromagnetic field of the porphin, without reducing or otherwise affecting the porphin. On the average, only one out of every n collisions between excited benzoin and unexcited porphin results in formation of an activated complex. However, we may safely say that practically every collision between excited benzoin and excited porphin results in an activated complex, for one paramagnetic molecule exerts such fields on another as to cause it to make the transition to the ground state.

We shall now calculate the steady-state concentration of excited benzoin. If F_b is the light absorbed by the benzoin, expressed in einsteins per liter per second, and a_b is the fraction of singlet excited benzoin molecules passing over into the triplet excited state, then the rate of formation of triplet excited benzoin is $a_b F_b$. Excited benzoin decays by three paths: (1) natural decay, with parameter τ_b and the rate B'/τ_b, where B' represents the concentration of excited benzoin; (2) collisions with ground-state porphin to form an activated complex; (3) collision with excited porphin.

To find the number of collisions, we must again draw upon gas kinetic theory, and obtain[38]

$$Z = 2\sigma_{12}^2 n_1 n_2 \sqrt{\frac{RT2\pi}{M}}$$

for the number of collisions between molecules of kinds 1 and 2 per cc per second, symbols and units as on Page 66. Multiplying this expression by $1000/N = \dfrac{1}{6 \times 10^{20}}$ gives the number of "moles of collisions" per liter per second. The rate of loss of excited benzoin by collision with ground-state porphin is then $\dfrac{Z}{n} \dfrac{1000}{N}$, remembering that only $1/n$ of these collisions is effective. The rate of loss by collision with excited porphin will be denoted by $Z'' \dfrac{1000}{N}$. Putting all these expressions together, and equating to zero:

$$\frac{dB''}{dt} = a_b F_b - \frac{B''}{\tau_b} - \frac{1000}{N} \frac{Z}{n} - \frac{1000}{N} Z'' = 0$$

Now $Z = 5.0(4 \times 10^{-8})^2 B'' \dfrac{N}{1000} P \dfrac{N}{1000} \sqrt{\dfrac{8.3 \times 10^7 \times 300}{162}} = 36 \times 10^{30} B''P$,

and similarly for Z''. The steady-state concentration of excited benzoin is therefore found to be:

$$B'' = \frac{a_b F_b}{\dfrac{1}{\tau_b} + \dfrac{6 \times 10^{10} P}{n} + 6 \times 10^{10} P}$$

Now the rate of reduction of porphin is connected with the number of collisions by the equation

$$\frac{-dP}{dt} = \left(\frac{\beta Z}{n} + \beta'' Z''\right) \frac{1000}{N},$$

where β is the fraction of activated complexes involving a ground-state porphin which lead to reduction, similarly β'' for complexes involving excited porphin.

The quantum yield has been previously defined as

$$\phi = \frac{1}{F_b} \frac{dP}{dt} \, .$$

Now substitute Z and Z'', and recall the still valid relationship $P'' = a_p \tau_p F_p$.

$$\phi = \frac{a_b \left(\frac{\beta}{n} P + \beta'' a_p \tau_p F_p\right)}{\dfrac{1}{6 \times 10^{10} \tau_b} + \dfrac{P}{n} + a_p \tau_p F_p} \, .$$

Now the essential independence of the quantum yield from porphin concentration implies that the term involving τ_b is small compared with the rest of the denominator. At least for the time being, we shall drop this term, and rearrange the expression for quantum yield to:

$$\phi = \frac{a_b \left(\frac{\beta}{n} + a_p \tau_p \beta'' \frac{F_p}{P}\right)}{\dfrac{1}{n} + a_p \tau_p \dfrac{F_p}{P}} \, .$$

Since F_p/P is the independent variable, a plot may be made of quantum yield against this variable; it is presented in Fig. 26. In general, the points scatter away from the main trend about as widely as they did on the simple linear plot presented in the last section, but three points have notably improved their position with respect to the others. The two points representing runs made with low porphin concentration and medium benzoin concentration, which before lay quite far above the straight line, are now seen to have moved to the extreme right of the graph, and lie much closer to the line drawn through the points. Also the point representing a run with both low porphin concentration and low light intensity, previously unreasonably high, has moved toward conjunction with the line. There is, perhaps, a slight tendency for points representing runs wherein the ratio of benzoin to porphin concentrations is high to fall low on the graph. This may be the result of a small self-quenching effect induced by repeated collisions of excited benzoin with normal benzoin molecules.

The expression for quantum yield involves three parameters, and may be written

$$\phi = \frac{a + bc(F_p/P)}{1 + c(F_p/P)}$$

where $a = a_b \beta$, $\tau_b = a_b \beta''$, and $c = n\tau_p a_p$. By minimizing the variance with respect to these parameters, it would be possible to find the best curve of this form through
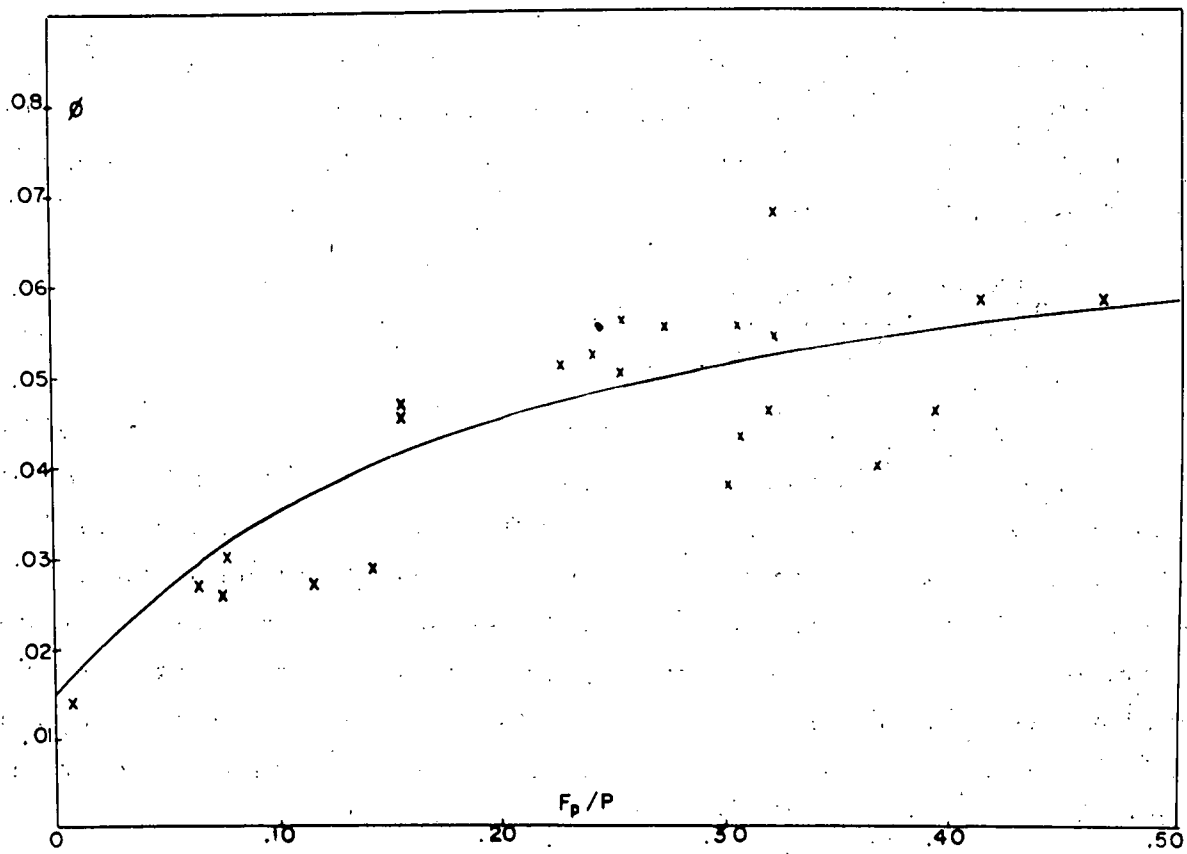
Fig. 26

the points. However, in this case, the data are plainly not of sufficient accuracy to make such a calculation profitable. A curve, which seems to represent the points pretty well, has been drawn on the graph, assuming reasonable values for the three parameters. The parameter a is the quantum yield at zero light intensity, and appears to have the value of 0.015; b is the quantum yield at infinite light intensity, and is assigned the value 0.075. A third point is needed to evaluate "c"; therefore we assumed the quantum yield is 0.045 when F_p/P is 0.20, giving a value for c of 5.8.

Let us see what these values for the parameters mean. We shall present evidence in the next section that a_b, the fraction of excited benzoin molecules passing into the triplet state, is about 0.2. Since $a = a_b\beta = 0.015$, $\beta = 0.075$, and this is the fraction of activated complexes involving ground-state porphin which lead to reduction. Similarly, $b = a_b\beta'' = 0.075$, so $\beta'' = 0.4$, and this is the fraction of activated complexes involving excited porphin which lead to reduction. The remaining parameter $c = na_p\tau_p = 6$. Suppose n = 1000, a reasonable number on the basis of our arguments on Page 67. Suppose also that $a_p = 0.5$, which is a generous estimate, but not unreasonably so. Then the lifetime for porphin $\tau_p = 0.012$.

There is another requirement on the value of n. Let us again write the expression for quantum yield, including this time the term in denominator which we had thence omitted.

$$\phi = \frac{a + bc\ F_p/P}{1 + c\ F_p/P + \dfrac{n}{6 \times 10^{10} P\tau_b}}$$

We now require that this term, which involves the decay parameter for benzoin and the concentration of porphin, be small compared to unity, in order that the quantum yield be practically independent of porphin concentration. Taking n = 1000, and $P = 5 \times 10^{-5}$, this term will be less than 1/3 if τ_b is greater than 10^{-3} seconds.

We cannot put much reliance in values of physical quantities found this way, but the fact that values may be chosen, each within the range of possibility, which enable a kinetic derivation of an experimental rate law, argues strongly for that derivation.

There is one matter that has not been mentioned so far: In the initial step of the reaction, the collision between excited benzoin and porphin, is one hydrogen atom or two transferred to the porphin? Almost all the reducing agents that affect porphin are of the enediol type or have related structure; two hydrogens are available from each molecule, and both are close together on the

molecule. However, n-hexyl mercaptan does show a slow photoreducing action, and this suggests that one-proton reductions are possible. If in fact the first step in all these reductions is a one-proton transfer, one may ask, what are the succeeding steps and is there any possibility that a chain reaction may be set up? A chain reaction mechanism would have two distinct advantages over the mechanism just presented. It would explain the high quantum yield without requiring high yield on the initial step, and explain away the scatter of the results in terms of trace inhibition or promotion.

For convenience in discussing certain chain mechanisms, we shall make a change in notation. Hitherto, the benzoin concentration has been denoted by "B". Henceforth, "B" will signify benzil , so benzoin will be "BH_2". Porphin will continue to be denoted by "P", and chlorin now by "PH_2". "PH" AND "BH" are the semiquinoid free radicals.
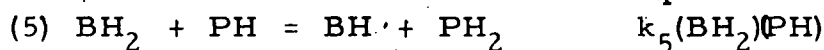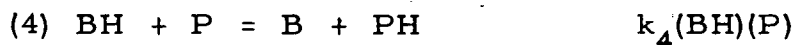
We consider two steps of excitation:

(1) BH_2 + light = BH_2" $k_1 F_b$

(2) P + light = P" $k_2 F_p$
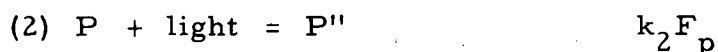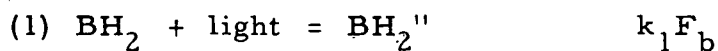
where double prime signifies the triplet state, and k_1 and k_2 are equal to the corresponding a's of the previous discussion. We introduce at this time one step of chain initiation:

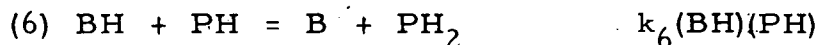(3) BH_2" + P = BH + PH $(k_3 + k_3'P)k_1 F_b$
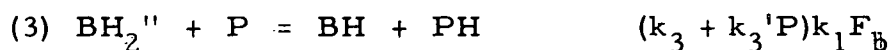
The meaning of the rate expression is: if $k_3' = 0$, every excited benzoin molecule will react with or be deactivated by a porphin molecule, so $k_3 = \beta$ of the previous discussion. If $k_3 = 0$, reactive collisions with porphin are so rare that a second-order reaction rate is applicable.
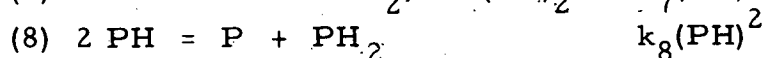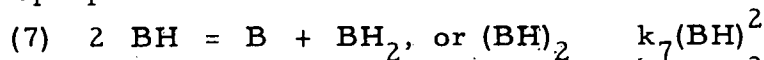
Two steps of chain propagation:

(4) BH + P = B + PH $k_4 (BH)(P)$
(5) BH_2 + PH = BH + PH_2 $k_5 (BH_2)(PH)$

Chain termination may be by:

(6) BH + PH = B + PH_2 $k_6 (BH)(PH)$

or by disproportionation:

(7) 2 BH = B + BH_2, or $(BH)_2$ $k_7 (BH)^2$
(8) 2 PH = P + PH_2 $k_8 (PH)^2$

Reaction (6) asserts that the reaction is exothermic; if it were not, benzoin and porphin would be regenerated, and the propagation steps would not go, since their sum is the net reaction. There is no sign of anything corresponding to $(PH)_2$ in the spectrum. This compound would have the symmetry of chlorin,

and presumably a strong band in the red.

Since excited porphin apparently does not react with ground-state benzoin, it must react either with B" or with BH. Assume the former, and the auxiliary initiation step:

(3') $BH_2" + P" = BH + PH$ $k_3"k_1k_2F_bF_p$
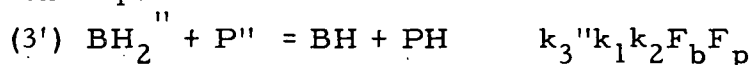
If we use all these reactions except (7) and (8), assume steady-state concentrations of BH and PH, and neglect the contribution of reaction (6) to the quantum yield (otherwise there would be no point having a chain), the quantum yield is found to be:

$$\phi = \sqrt{\frac{k_1k_4k_5}{k_6} \frac{(P)(BH_2)}{F_b} (k_3 + k_3' + k_3"k_2F_p)}$$

Other things being equal, the quantum yield decreases with increasing light intensity, contrary to the experiment.

If we hobble the propagation by assuming that one or both of steps (4) and (5) not go, we have no chain at all, and the quantum yield $\phi = k_1\left[k_3 + k_3'(P) + k_3"F_p\right]$ is just what we would have obtained if no thought of chain reactions or one-proton reductions had arisen. It is impossible to distinguish kinetically between such a sequence of reactions as (3), (3'), (4), (6), and (8) and a simple two-hydrogen transfer.

The remaining possibility is that excited porphin enters the propagation steps. The only viable chain we can find makes use of the step:

(4') $BH + P" = B + PH$ $k_2k_4' (BH)F_p$
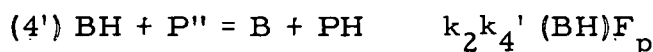
along with steps (3), (5), and (6). The quantum yield is found to be:

$$\phi = k_1\left[k_3 + k_3'(P)\right] + \sqrt{\frac{k_1k_2k_4'k_5}{k_6} \frac{k_3 + k_3'(P)) (BH_2) F_p}{F_b}}$$

and is seen to be independent of light intensity, contrary to experiment. No chain, then, seems to be discoverable which explains the dependence of the quantum yield on light intensity. Basically, the trouble is that increasing the light intensity increases the concentrations of free radicals, and thereby increases the rate of the termination steps.

Concluding Remarks

In view of the mechanism we have settled on, it might be expected that copper porphin would also be reduced by benzoin, and that the quantum yield would be independent of the amount of light absorbed by the porphin, for copper porphin has no fluorescence of triplet excited state. This seems to be the case; the quantum yield found in such a run was 0.0053, and appeared to be independent of light intensity, when that factor was varied. The quantum yield

is about one-fourth the minimum quantum yield for reduction of zinc porphin. No rate run was made on nickel porphin, but in sunlight it seems to be reduced about as fast as the copper complex, which is consistent with the fact that nickel porphin has no phosphorescence or fluorescence.

One of our original intentions was to measure the dependence of reaction rate on concentration of base, and indeed, the first experiments were directed to this end. These runs are not included, since owing to an oversight, quantitative conclusions could not be made. The base used was gamma-collidine, 2, 4, 6-trimethylpyridine[*], because it is not so strong as to stop the reaction complete-ly when present in small amounts $(K = 2 \times 10^{-7})$, not overly volatile at the tem-perature of flushing with nitrogen (b.p. 171°), and not quickly discolored in air. It appeared that it was possible to put in at least ten times as much base as is necessary to complex the porphin completely without affecting the reduction rate appreciably. Complexing the porphin appears not to affect reduction rate, so the eventual retardation of reduction rate by excess of base must be a solvent effect. Perhaps the lifetime of excited benzoin is shortened in basic solution.

The scattering of results is such as to make a discussion of errors almost superfluous. As far as instrumental error is concerned, the main limit on our accuracy was the reproducibility of the Cary spectrophotometer tracing. Since the primary measurements were differences in optical densities, random wan-dering of the Cary recorder needle often amounted to more than 10 percent of the nonuniformity of the rate during a run, and sometimes made it very difficult to extrapolate satisfactorily to zero. We know that the presence of oxygen enables a side reaction by which porphin is destroyed, and that this reaction is faster than the reduction. Since the reduction rate was measured by following the fall of the porphin band, this effect makes the apparent rate too fast. Since a trace of oxygen was always present, the main purpose of extrapolation was to by-pass the early points of the graph where oxygen was being consumed. But oxidative destruction of porphin produces compounds having absorption in the region where benzoin absorbs, and since the initial amount of light absorbed by the benzoin was calculated from the initial concentrations, the extrapolation would yield an initial rate that is too low. In each separate case, using the observed rates as a guide, it was necessary to use judgment in selecting the initial rate.

An imponderable effect of oxygen is its ability to quench phosphores-cence, or deactivate molecules in their triplet excited states. In our reactions, the effect would be to slow down the reduction rate at the first.

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[*]   Suggested by Dr. H. Rapoport.

KINETICS OF THE BENZOIN-CATALYZED DESTRUCTIVE
OXIDATION OF ZINC TETRAPHENYLPORPHIN

We have already discussed how benzoin accelerates the rate at which porphin combines with oxygen. It was soon decided to investigate the kinetics of this reaction, both for its own sake and for whatever light it may shed on the mechanism of the benzoin reduction of porphin.

The physical setup was the same as that for the reductions, except that the tubes were not flushed with nitrogen or evacuated, and the spectra were taken from 570 to 490 mμ. The first experiment was allowed to run to completion so that the absorption curve of the oxidation product or products could be obtained. Knowing this spectrum, and the spectrum of zinc porphin, we could convert optical densities into concentrations in a way similar to that used in the reduction experiments. The peak of the spectrum of the oxidation product was at 525 mμ; the optical densities at 550 and 520 mμ were used for calculation. These are denoted by D_{550} and D_{520}, the density at 550 due to porphin alone by D_p, and the density at 520 due to oxidation products alone by D_o. An examination of the spectra shows that

$$D_{550} = D_p + 0.68 D_o \text{ and}$$

$$D_{520} = 0.135 D_p + D_o.$$

Rearrangement yields:

$$D_p = 1.09 (D_{550} - 0.68 D_{520}) \text{ and}$$

$$D_o = D_{520} - 0.135 D_p.$$

Although we do not need it to study this reaction, the extinction coefficient of the oxidation product at 520 mμ may be obtained by comparing the initial rate of rise at this wave length with the rate of fall of absorption at 550 mμ. The average of four runs is $9.3 \pm 0.2 \times 10^3$ at 520 mμ, which means a value of 9600 at the peak, 525 mμ.

Runs were made in which the benzoin concentration, porphin concentration, light intensity, wave length, and oxygen pressure were varied. The initial rate of porphin loss was found, the light absorbed by the benzoin found as described before, and the quantum yield calculated as before. The results of the run are presented in Table IX.

During run No. IV, the light intensity was reduced by means of a wire gauze screen in front of the aperture for the first 35 minutes, and the rate compared with that when the screen was removed. The fall in optical density of porphin at 550 mμ is plotted against time in Fig. 27. The ratio of low to high

light intensities was found to be 0.327; the corresponding ratio of the rates was 0.331, establishing linearity with light intensity.

Porphin, as we have mentioned before, by itself in solution and in the presence of air and light, is slowly destroyed, taking apparently about the same path as when benzoin is present. The rate of destruction was determined, in order that a correction might be made, so that only the benzoin-catalyzed oxidation be considered. The quantum yield of oxidation of porphin alone was found to be 1.05×10^{-4}, based on light received by the porphin.

That only light received by the benzoin is required in the benzoin-catalyzed oxidation was shown by use of filter No. 3385, under which no more reaction occurred than could be accounted for by porphin's own absorption and by use of filter No. 5970, with which it was shown that, within the experimental error, the reaction rate is proportional to the amount of light received in the 3650 Å line.

A glance at the table of results shows that the quantum yield is independent of benzoin concentration, or porphin concentration, and of oxygen pressure. In Fig. 28 are shown plots of porphin optical density against time, during some of the runs. The rate is seen to be practically constant during each run, which indicates a zero-order dependence on porphin concentration. Owing to formation of oxidation products of porphin, the optical density at 3650 Å rises slowly during the reaction, accounting for the tapering off of the rate as the reaction proceeds.

For most of the runs, the partial pressure of oxygen over the solution was 1/5 atmosphere, obtained simply by letting the tubes stand in air. For the run VII, pure oxygen was bubbled through the tube for fifteen minutes, to insure a partial pressure five times as large. No change in the quantum yield was noted. The average quantum yield of the reaction is 0.103, and the standard deviation is 0.011, which is about the range of experimental error.

The interpretation of this reaction rests upon a paper recently published by Schenck.[41] He discusses quite a few photochemical reactions of double-bonded compounds, and presents evidence that they go through an excited triplet state. Among other things, he presents a mechanism for sensitized oxidations. The first step in such a reaction is absorption of light by the sensitizer, and transition from the singlet to the triplet state:

$$S + light = S', \qquad S' = S''.$$

The sensitizer then collides and reacts with oxygen to form a diradical:

$$S'' + O_2 = \cdot SO_2 \cdot$$
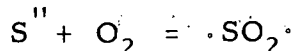
which, upon collision with the molecule to be finally oxidized, transfers its oxygen to that molecule:

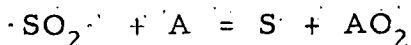$$\cdot SO_2 \cdot + A = S + AO_2$$

TABLE IX

Rate Run Results: Benzoin-Catalyzed Degradative Oxidation of Porphin

Run. No.	Porphin conc. molar	Benzoin conc. molar	O_2 pressure atm.	Init. rate moles/sec.	F_b, $\dfrac{einsteins}{sec \cdot liter}$	Quantum yield
I	5.5×10^{-5}	7.2×10^{-3}	0.2	1.46×10^{-8}	13.0×10^{-8}	0.112
II	4.35 "	3.15 "	0.2	0.63 "	6.4 "	0.098
III	4.2 "	17.1 "	0.2	3.0 "	26.2 "	0.115
IV	4.5 "	10.1 "	0.2	0.64 "	6.0 "	0.107
V	2.3 "	7.4 "	0.2	1.64 "	16.7 "	0.098
VI	6.65 "	9.1 "	0.2	1.21 "	15.3 "	0.079
VII	4.9 "	9.1 "	1.0	1.84 "	18.0 "	0.102
VIII	4.25 "	1.57 "	0.2	0.38 "	3.4 "	0.112
						Ave. 0.103 ±0.011
	Cu porphin					
IX	5.4 "	10.4 "	0.2	3.75 "	21.5 "	0.174

Light Intensity Dependence of

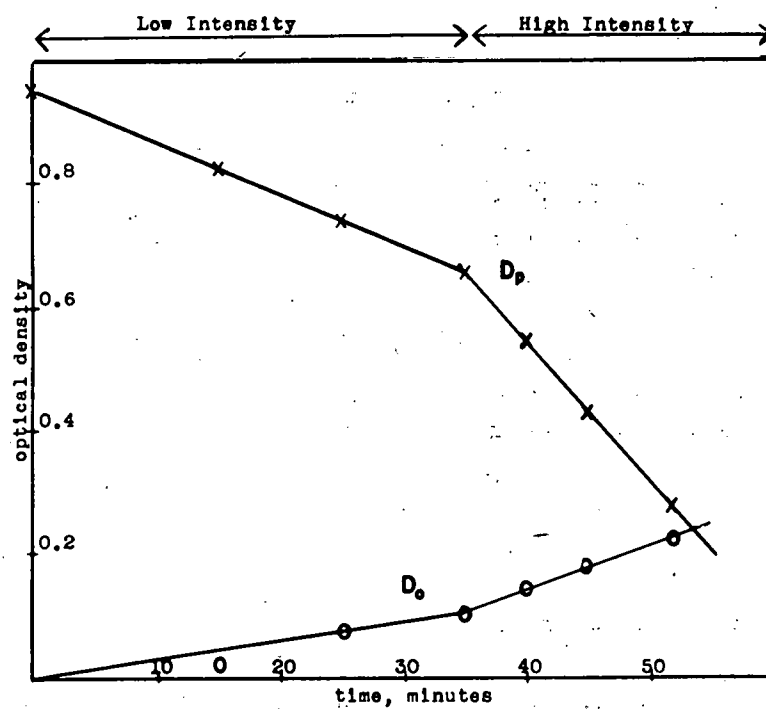Benzoin Catalysed Degradative Oxidation

of Zinc Tetraphenylporphin

Fig. 27

Benzoin Catalysed Degradative Oxidation of Zinc Tetraphenylporphin:

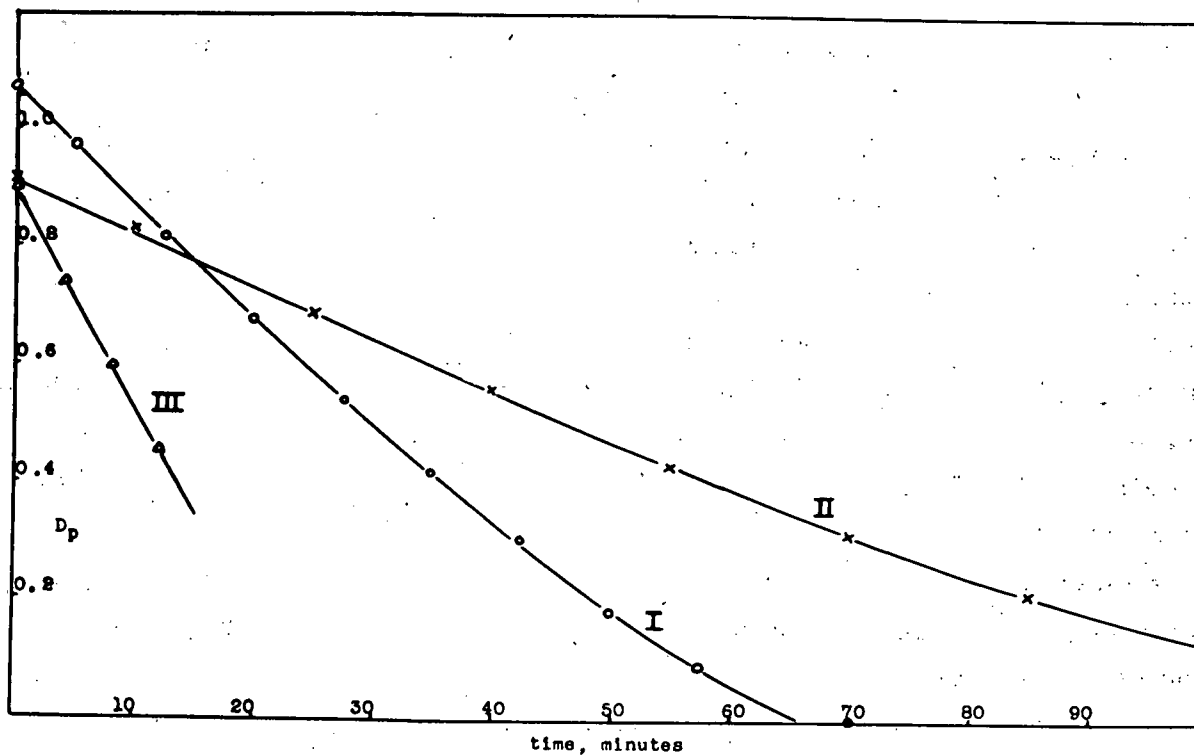Fall of Optical Density of Porphin during Three Runs

Fig. 28. Numerals refer to Table IX.

In our reaction, benzoin is the sensitizer, porphin the molecule finally oxidized. Since the concentration of oxygen in the reaction solutions is some-what larger than 10^{-3} molar,[*] triplet excited benzoin has ample opportunity to react with oxygen before decaying, judging from our previous calculations of time between collisions. Every benzoin in the triplet state reacts, then, with oxygen, to form a peroxide, perhaps of the following structure,

$$C_6H_5-\underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{\overset{|}{O}-O}{\overset{O}{\underset{|}{\overset{\|}{C}}}}-C_6H_5$$
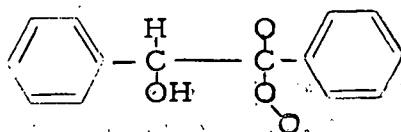
which is stable enough to last until a reactive collision with a porphin molecule. The quantum yield would, under these conditions, be practically independent of benzoin, oxygen, or porphin concentrations, as is actually observed.

One of the stronger pieces of evidence that benzoin has an easily accessible long-lived triplet state is that it shares catalytic oxidative ability with benzil, acetophenone, anthracene, phenanthraquinone, and other compounds. The abil-ity of anthracene to form an endoperoxide is well known. Benzil, under the influence of light, can add to double bonds, forming dioxene derivatives. Phen-anthraquinone can add to double bonds, aldehydes, and sulfur dioxide under the influence of light. These reactions are taken by Schenck to be evidence of the mediation of a triplet state.[41]

It is interesting to note that copper porphin is destroyed more rapidly than zinc porphin by benzoin and air, which precludes any possibility of partic-ipation of photo-excited porphin in the reaction. The quantum yield was 0.17. The upper limit of quantum yields of this type of reaction is the fraction of singlet excited molecules making the transition to the triplet state, denoted by α in the last section. If we take the quantum yield of the oxidative destruction of copper porphyrin to be close to this maximum, we obtain the value of α_b used in the last section.

One problem remains in connection with this work: What are the structures of the compounds formed by oxidation of porphin? Unfortunately, we can do nothing but make a few suggestions. The compound with the high peak at 463, which appears during reductions with benzoin, is apparently the only one with a Soret band, which implies that the great ring of eighteen carbons and nitro-gens is still conjugated. The compound or compounds with peak of absorption from 490 to 530 mμ, which appear under various conditions of oxidation, have not the band structure characteristic of porphyrins, and therefore have some-

[*] Cf. International Critical Tables, on Solubilities of Gases in Liquids, 3, p. 262.

where suffered addition across the great ring, perhaps at the bridge positions. The following endoperoxides are possible primary oxidation products.
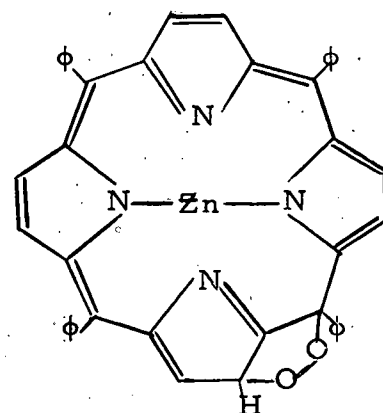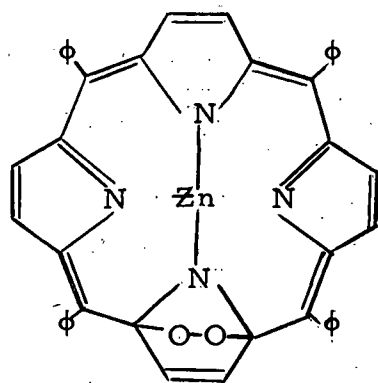
KINETICS OF THE OXIDATION OF ZINC
TETRAHYDROTETRAPHENYLPORPHIN BY
PHENANTHRAQUINONE

The secondary purpose of this thesis is the identification and characterization of the principal reduction product of porphin, the compound we have called zinc tetrahydrotetraphenylporphin. Dorough and Huennekens studied the oxidation of zinc chlorin (dihydroporphin) by quinones; we decided to try a few oxidation experiments, to see if the mechanism would be the same as that for chlorin oxidation. A secondary reason was to obtain the extinction coefficient of the tetrahydroporphin at 604 mμ, by comparing the rate of fall of that band with the rate of rise of the porphin band of known extinction coefficient.

The quinone chosen for the runs was phenanthraquinone; a solution in benzene was made up, of concentration 8.0×10^{-3} molar, using quinone which had been recrystallized from alcohol and benzene. Zinc tetrahydroporphin was prepared according to the directions given in the section on reduction by dihydroxyacetone. After extraction seventeen times with water, and drying, the benzene solution was made up to volume in a 25-cc. volumetric flask, flushed thoroughly while cold with nitrogen, and stored under nitrogen in the dark.

The apparatus used was the same as that used for the reduction experiments, and the tubes were, of course, flushed with nitrogen and evacuated to get rid of the oxygen. None of the mercury lines is strongly absorbed by the tetrahydroporphin, so the mercury sunlamp was replaced by an incandescent 300-watt G.E. reflector spotlight. Irradiation was carried out under filter No. 3480, which passes the high peak at 604 mμ but cuts out light absorbed by the porphin and by the quinone. The output of the lamp, in watts per mμ, in the vicinity of 600 mμ, was measured by comparing the flux passed by filter No. 3480 with that passed by No. 2412, and is subject to an error of about 10 percent which is carried over to the accuracy (but not precision) of the quantum yield. It had been possible, when using the mercury lamp, to measure directly the amount of light absorbed by the porphin as a function of concentration, but this was not possible now, because of the large amount of radiation in the red and infrared which is not conveniently filtered out. Instead, from the spectrum of the tetrahydroporphin, plots are made at various concentrations of the fraction of light absorbed by the tetrahydroporphin, multiplied

by the transmission of filter No. 3480, against wave length from 570 to 640 mμ.
The area under one of these curves, when multiplied by the output in watts per
millimicron, gives the flux in watts absorbed by tetrahydroporphin at that
concentration. The areas of the curves are plotted as a function of concentra-
tion, so that the flux absorbed may be found for any solution. For the actual
calculations and graphs, the optical density of the solution at 604 mμ is substi-
tuted for the concentration, since the latter was unknown but proportional to
the former. Fig. 29 shows a plot against optical density of the number which
multiplies flux per millimicron to give flux absorbed when filter No. 3480 is
imposed.

The first problem was to calculate the extinction coefficient of the tetrahy-
droporphin at 604 mμ, so that its concentration might be known. This calcula-
tion is in no way dependent on the reaction rate, but depends only on the abso-
lute values of fall and rise of tetrahydroporphin and porphin bands. Unfortun-
ately, the seventeen washings did not get out all the pyridine, or else a trace
was accidentally introduced, because the appearance of the porphin spectrum
was such as to indicate that it was about half complexed with base. The band
maximum was at about 555 mμ, instead of 550 for benzene or 563 for pyridine.
When the band maximum was at 555 mμ the extinction coefficient at that wave
length was found to be 16,500. The average, over sixteen intervals in three
runs, of the ratio of tetrahydroporphin to porphin band heights was 3.60. The
median was 3.52. The standard deviation of the samples from the mean was
0.96, so the standard error of the mean was $0.96/\sqrt{16} = 0.24$. Using the mean
value, the extinction coefficient of tetrahydroporphin at 604 mμ is $59 \times 10^3 \pm 4$.
Difficulty in reading the spectra accounts for the lack of precision.

Three runs were made, using different quinone concentrations; the results
are summarized in Table X. The calculation reducing observed optical den-
sities to concentrations was particularly wretched for these runs, owing to the
mentioned presence of porphin both in base-complexed and uncomplexed forms,
and so will only be sketched. Optical densities are read at 530, 555, 604 and
650 mμ. The optical density of the tetrahydroporphin at 604 mμ is $D_{604} - D_{650}$,
which corrects for "background", minus a small(and actually negligible) cor-
rection for absorption by base-complexed porphin. An optical density charac-
teristic of the zinc porphin is not necessary for a quantum-yield investigation,
but is necessary for the work described in the preceding paragraph. From
the spectra of porphin in benzene and pyridine, a ratio can be found of the
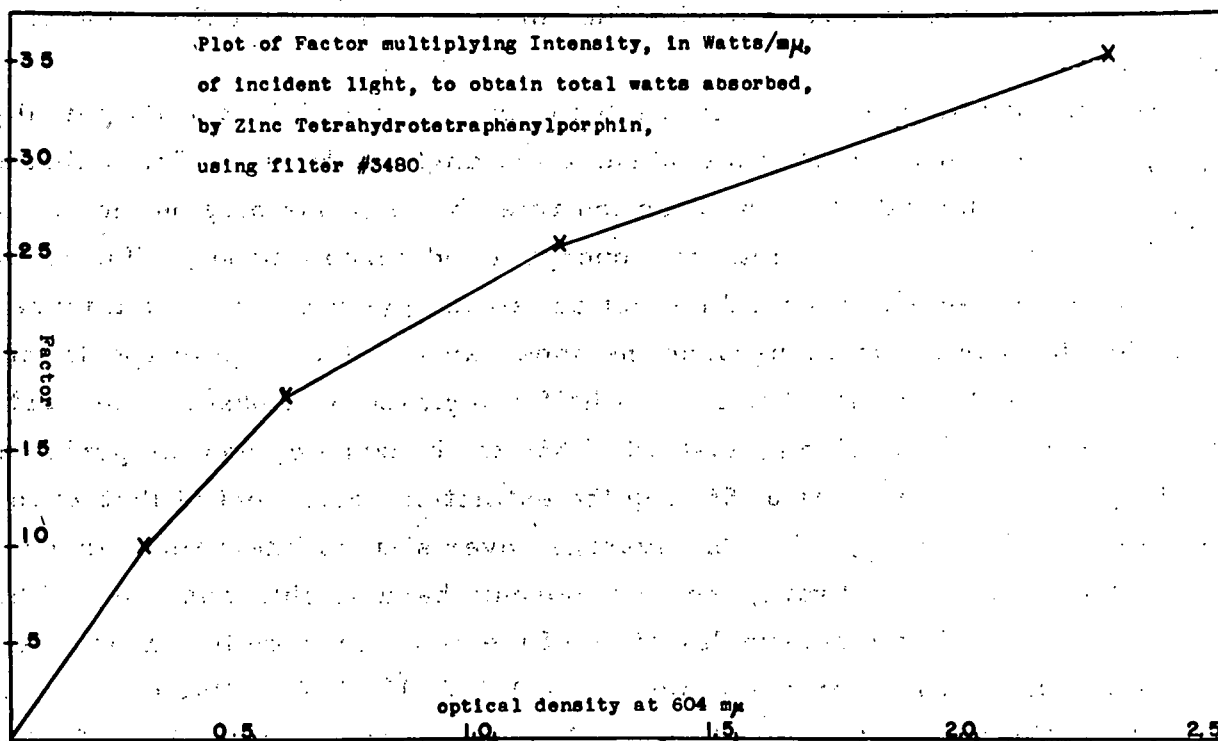optical density at 555 mμ due to porphin alone, and the difference between the

Plot of Factor multiplying Intensity, in Watts/mμ,
of incident light, to obtain total watts absorbed,
by Zinc Tetrahydrotetraphenylporphin,
using filter #3480

optical density at 604 mμ

Fig. 29

TABLE X

Oxidation of Zinc Tetrahydrotetraphenylporphin by Phenanthraquinone

First Rate Run

THPorphin conc.: 2.8×10^{-5} molar

Phenanthraquinone conc.: 2.5×10^{-4} molar

Interval	Duration mins.	Light abs einsteins/1/sec.	Oxid. rate moles/sec.	Quantum yield
I	10	2.02×10^{-5}	7.2×10^{-9}	3.6×10^{-4}
II	11	1.87 "	7.3 "	3.9 "
III	12	1.66 "	5.4 "	3.3 "
IV	12	1.44 "	4.8 "	3.3 "
V	15	1.24 "	3.7 "	3.0 "
VI	20	0.90 "	2.5 "	2.8 "

Second Rate Run

THPorphin conc.: 2.90×10^{-5} molar

Phenanthraquinone conc.: 2.46×10^{-5}

I	10	2.04×10^{-5}	8.6×10^{-9}	4.2×10^{-4}
II	10	1.93 "	7.3 "	3.8 "
III	10	1.70 "	5.35 "	3.15 "
IV	11	1.56 "	2.9 "	1.86 "
V	15	1.47 "	1.22 "	0.83 "
VI	24	1.42 "	0.65 "	0.46 "

Third Rate Run

THPorphin conc.: 3.1×10^{-5}

Phenanthraquinone conc.: 2.9×10^{-3}

I	10	2.10×10^{-5}	7.5×10^{-9}	3.6×10^{-4}
II	15	1.92 "	5.6 "	2.9 "
III	15	1.71 "	5.5 "	3.2 "
IV	15	1.48 "	3.75 "	2.5 "
V	15	1.31 "	3.3 "	2.5 "
VI	15	1.13 "	2.1 "	1.9 "

Oxidation of Zinc Tetrahydrotetraphenylporphin

by Phenanthraquinone in Benzene:
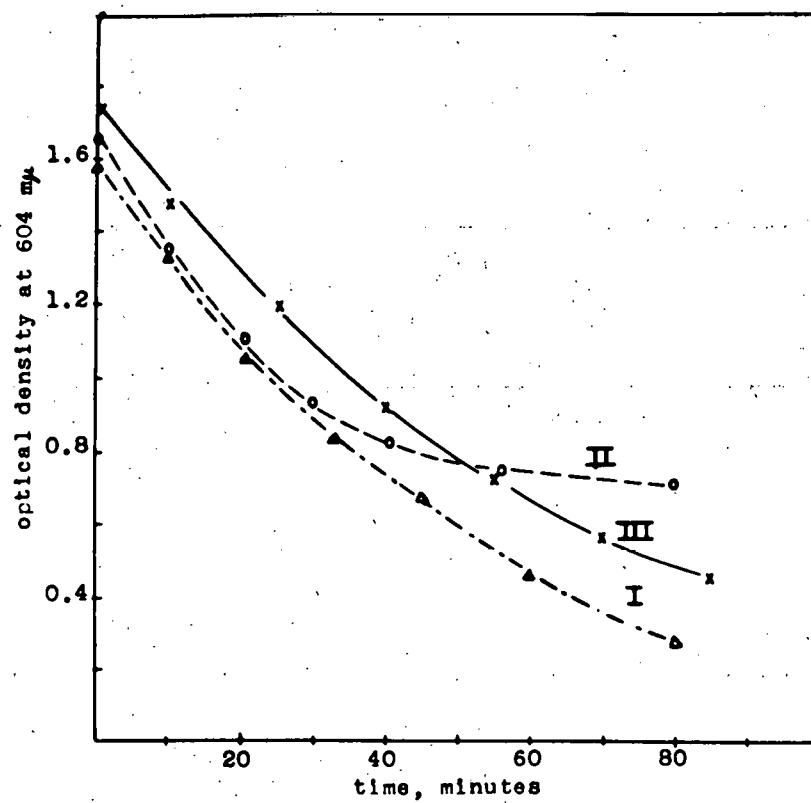
Fall of Tetrahydroporphin Band

Fig. 30. Numerals refer to Table X.

Oxidation of Zinc Tetrahydrotetraphenylporphin
by Phenanthraquinone in Benzene:
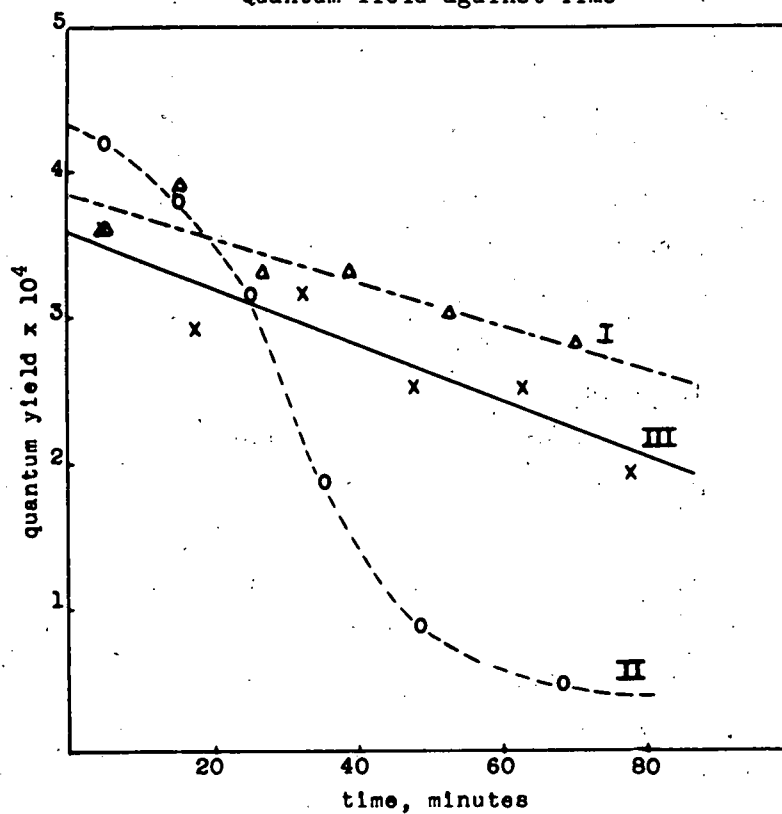Quantum Yield against Time

Fig. 31

observed densities at 555 and 530 mμ, after this undergoes a small correction

for "background" and for absorption due to the tetrahydroporphin. In fact

$$D_p = \frac{1}{1 - 0.24} \ (D_{555} - D_{530} - 0.13 \ D_t)$$

using notation defined when dealing with reduction of porphin.

The initial concentrations of quinone cover a hundredfold range. It can be seen from the tables that the quantum yield is independent of quinone concentration over this range, except for perhaps a small decrease at high quinone concentrations, possibly a solvent effect on the tetrahydroporphin excited-state half-life.

The rate of fall of the tetrahydroporphin band is found, converted to concentration change using 5.9×10^4 as extinction coefficient, and divided by the light absorbed, to give quantum yield.

It will be noticed that, in the first and third runs, the quantum yield remains fairly constant during the run, which indicates independence of tetrahydroporphin concentration, and of light absorbed by the tetrahydroporphin. True, the yield appears to drop off as the run progresses, but we believe that this is due to our neglect of light absorbed by porphin and other materials in the region from 570 to 640 mμ. Correction for this, which becomes progressively larger as the amount of tetrahydroporphin becomes smaller, would decrease the value for light absorbed by the tetrahydroporphin and thereby raise the quantum yield.

These results indicate that the oxidation of tetrahydroporphin by quinones follows the same rate law, and probably the same mechanism, as does the oxidation of chlorin: the tetrahydroporphin molecule, excited to a triplet state, deposits its hydrogens upon a nearby quinone.

The second run of the series is interesting, for here the phenanthraquinone concentration is about the same as the tetrahydroporphin concentration. In Fig. 30 the fall of the tetrahydroporphin band for this run is compared with the decay during the first and third runs; in Fig. 31 the quantum yields for the three runs are plotted as functions of time. The quinone runs out when the reaction is about half done.[*] The quantum yield begins high, a little higher than the others, it would seem, but soon drops rapidly to zero. This means, in terms of our mechanism, that the quinone concentration is so low that a triplet-state tetrahydroporphin molecule is no longer sure of reacting with a quinone molecule before decaying to the ground state. It might be expected that a study of this

[*]   It should have run out just before the reaction was half done; the extra tetrahydroporphin oxidized is due to the presence of oxygen, the effect of which has not been considered in the calculations. This run is, incidentally, a bit of fairly good evidence that the compound is a tetrahydroporphin.

decay would give us some information about the decay parameter of zinc tetra-hydroporphin.

Let us postulate a reaction mechanism similar to that used for discussion of the reduction. An excited tetrahydroporphin molecule collides with quinone without damage a number of times, n, on the average, before forming an acti-vated complex, after which it is either oxidized or becomes deactivated. Our premises, and therefore our expression for quantum yield, will be exactly the same as in the theoretical treatment of reduction, if we leave out of the equa-tion on Page 69 the terms concerning triplet-triplet collisions, use the letter Q for the quinone concentration, and change and collect a few constants:

$$\phi = \frac{aQ}{Q + \frac{n}{\tau \times 10^{-10}}}$$

Now when Q is large, the quantum yield is constant at about 4×10^{-4}, so

$$\phi = \frac{4 \times 10^{-4}Q}{Q + \frac{n}{\tau \times 10^{+10}}}$$

Now referring to the graph of optical density against time, we may extrapolate to infinite time, where the quinone concentration is zero, and find the residual tetrahydroporphin concentration. We now choose the point where the quantum yield is 2×10^{-4} so that $Q = \frac{n \cdot 10^{-10}}{\tau}$, and find the tetrahydroporphin concentra-tion at this time. Twice the difference will be the quinone concentration at this time, and $Q = 8 \times 10^{-6}$. Therefore,

$$8 \times 10^{-6} = \frac{n \cdot 10^{-10}}{\tau}, \text{ or } \tau = n \times 2 \times 10^{-6}. \text{ If for example } \tau = 10^{-3},$$

then n = 500.

SUMMARY

This research was undertaken in an attempt to find and study reductions of porphin and chlorin that might be significant to photosynthesis. In this, we have failed. The reductions of porphin (and of chlorin, too) which we have found are much too slow to be of much service to photosynthesis, barring modifying circumstances. Worse, in contrast to the oxidations by quinones, the reductions seem to require light absorbed by the reducing agent. This has been demonstrated in the case of benzoin; for the other reducing agents, we have no quantitative data, but only the observation that these reductions only seem to proceed in bright sunlight, rich in ultraviolet light, and not in diffuse daylight or incandescent light sources, poor in ultraviolet light. The light requirements for reduction of zinc chlorin are still unknown, however. One qualitative run on reduction of zinc chlorin by ascorbic acid appeared to proceed in sunlight shone through the red filter No. 3480, but there may have been diffused unfiltered sunlight. This question remains open, and a worthy subject for future investigations.

The most pressing question opened up by these results is why low-energy light absorbed by the chlorin is sufficient for its oxidation, while high-energy light absorbed by the benzoin is required to reduce porphin. Is this simply a matter of energetics, of energy activation, or is it the result of some more subtle "steric" effect involving electron distributions in excited states?

Let us, finally, summarize the results of preceding parts of the thesis. We have found several reducing agents that in light reduce zinc tetraphenyl-porphin to chlorin and tetrahydroporphin, and have studied the kinetics of one such reduction, that by benzoin. The reaction rate was found to be directly proportional to the amount of light absorbed by the benzoin, but dependent on light absorbed by the porphin in such a way as to require a mechanism in which triplet excited-state benzoin molecules react both with ground-state porphin and with triplet excited state porphin. The latter accounts for about two-thirds of the reaction at high light intensities, when the quantum yield -- based on light absorbed by the benzoin -- is about 0.05. This reaction seems so far to be unique in requiring collisions between two different photo-excited molecules. This reaction is inhibited by base, but the reason is unknown, although possibly it is a shortening of the lifetimes of the photo-excited molecules.

By use of dihydroxyacetone in alcohol and pyridine, it is possible to prepare zinc tetrahydroporphin in good yield -- about 60 percent -- pure enough for spectral measurements and as a source material for experiments on its

oxidation. Its photo-oxidation by phenanthraquinone has been studied; it is oxidized smoothly and quantitatively to the porphin. The mechanism is the same as that for oxidation of chlorin, the reaction rate being proportional to the amount of light absorbed by tetrahydroporphin, but the quantum yield is rather low, around 4×10^{-4}.

The degradative oxygenation of zinc porphin has been further investigated. From zinc porphin and oxygen in benzene solution and sunlight, new oxygenation products have been generated and described. Degradative oxygenation has been found to be catalyzed by benzoin, benzil and many other compounds. The mechanism has been briefly studied in the case of benzoin catalysis. The reaction rate depends only upon the amount of light absorbed by the benzoin, and a mechanism presented by Schenck has been proposed for the reaction, involving transfer of oxygen from a benzoin-oxygen complex to porphin.

CORRELATIONS OF SPECTRA AND STRUCTURES OF PORPHYRINS

We have left until the last a discussion of certain problems involving spectra and structures of porphyrins, in order not to break the continuity of the treat- ment of reaction mechanisms, and also in order to have at our disposal as much information as possible about the chemistry of porphyrins. Two structural prob- lems have been deferred until now: the positions of the four "extra" hydrogens in tetrahydroporphin, and the characterization of the "hexahydroporphin." Con- sideration of these two problems will be found relevant to the chemistry of bacteriochlorophyll, and at the conclusion of this section, we shall propose a new structure for bacteriochlorophyll which seems best to fit the evidence avail- able.

Electronic Structure of Metal Porphyrin

Our attention must, however, be turned first to a problem that seems not to have attracted much attention in the literature, although there are a few ref- erences around the subject. The spectra of free-base tetraphenylporphin and its metal complexes seem to indicate that the absorption bands arise from the same electronic transitions, and that only vibrational transitions change in relative intensity. In fact, there is an almost continuous transition in the spectra as we pass through a series beginning with the free base, continuing with the metal complexes Cs_2, K, Na, Li, Mg, Cd, Zn, and terminating with Cu and Ni.[9] As might be expected, the metal in the center of the ring considerably alters the vibrational pattern, usually enhancing bands in the red region at the expense of bands in the blue.

But the transition-group metal ions bring into the ring with them many more electrons than alkali or alkaline earth metals-- electrons that are as- signed to the d shell, and which, being loosely held, are available for bonding, both with the sigma bond system, symmetric with respect to the plane of the ring, and with the pi bond system, antisymmetric with respect to the plane of the ring. Complexes such as nickel porphin apparently owe their stability to the presence of bonding d orbitals in Ni^{++}, whereas the lability of magne- sium porphin may be traced to lack of such. Still considering the sigma bond- ing between the metal and the nitrogens, a transition-group metal like nickel may be bonded equally to all four nitrogens by use of sp_2d hybrid bonds; but magnesium or calcium, lacking low-energy d orbitals, can form only sp hybrids which link them to only two nitrogens at a time. The symmetry of the ring, and resonance theory, however, require them to be linked to all

four nitrogens equivalently. We seek to replace the inadequate valence-bond description of these sigma bonds by a molecular orbital description valid for transition-group metals and alkaline earths alike.

Returning to the pi electron bond system, Zn^{++} for example, introduces three energy levels and four electrons into the energy-level ladder. The problem arises as to where we can assign these extra electrons and extra levels so that the term diagram remains unchanged in the vicinity of the transition.

The first step in these calculations is to separate the five 3d orbitals according to their character with respect to reflection in the plane of the porphyrin molecule (the xy plane). The angular dependences of an orthonormal set of d-functions are given by Pauling.[35] Two of them,[*]

$$d_{y+z} = (15)^{1/2} \sin\theta \cos\theta \cos\phi \text{ and}$$

$$d_{x+z} = (15)^{1/2} \sin\theta \cos\theta \sin\phi,$$

are antisymmetric with respect to the xy plane, and belong with the pi bonding system. The other three,

$$d_z = (5/4)^{1/2} (3\cos^2\theta - 1),$$

$$d_{x+y} = (15/4)^{1/2} \sin^2\theta \sin^2\phi, \text{ and}$$

$$d_{xy} = (15/4)^{1/2} \sin^2\theta \cos^2\phi,$$

are symmetric and belong with the sigma bonding.

In addition to the d orbitals, all ions bring s and p orbitals -- 4s and 4p in the case of zinc -- of which the s, p_x, p_y are symmetric and the P_z antisymmetric with respect to the plane of the ring.

We shall now sketch a simple molecular orbital calculation for the sigma bonding in the center of the ring for a porphyrin, such as zinc tetraphenylporphin. Put the nitrogen atoms on the x and y axes, and number them, as in the accompanying diagram (Fig. 32). Let their orbitals that are symmetric to the plane (essentially sp_2 hybrids) be labeled s_1, s_2, s_3 and s_4. The spatial relationship of these with the metal s (designated by s_o), p, and d orbitals is also illustrated. In accordance with the requirements of the symmetry group of the system, D_{4h}, we form the set of mutually orthogonal and normalized orbitals:

---

[*] Notation is that usually used for spherical coordinates: θ is the angle measured from the positive z axis, ϕ is measured from the x to the y axis.

$$S_1 = 1/2 \ (s_1 + s_2 + s_3 + s_4)$$

$$S_2 = 1/2 \ (s_1 - s_2 + s_3 - s_4)$$

$$s_3 = 1/2^{1/2} \ (s_1 - s_3)$$

$$s_4 = 1/2^{1/2} \ (s_2 - s_4)$$

These orbitals, together with the metal orbitals, fall into the following orthogonal representations:[*]

A: d_z, s_o, S_1

B_1: $d_x + y$

B_2: d_{xy}, S_2

E: P_x, S_3; P_y, S_4

The last representation is degenerate; the pairs chosen are orthogonal to each other. We wish to form, in each class, linear combinations of the orbitals, which will be orthogonal, and find their energies.

Representation A: The secular equation reads[**]

$$\begin{vmatrix} H_d - W & O & 2Bd_z \\ O & H_s - W & 2B_s \\ 2Bd_z & 2B_s & H - W \end{vmatrix} = 0$$

where W is the energy, $H = \int s_1 \overline{H} s_1$, $H_s = \int s_o \overline{H} s_o$, $Hd = \int d_z \overline{H} d_z$, $Bd_z = \int d_z \overline{H} s_1$,

$B_s = \int s_o \overline{H} s_1$, H being the Hamiltonian operator. Multiplicity of valence among the transition-group elements indicates that approximately $H_d = H_s$, and in any case, B_{dz} is small, owing to poor overlap between d_z and s_1 orbitals. Using these approximations, and letting $H_s - H = H_d - H = A_d$, the energy eigenvalues are:

$$W_1 = H_d$$

$$W_2 = \frac{(Hs + H)}{2} - 1/2 \sqrt{A_d^2 + 16B_s^2 + 16B_{dz}^2}$$

---

[*] Group and representation notation is meant to agree with that used by Margenau and Murphy, Mathematics of Physics and Chemistry, Chapter 15.

[**] Solution of the eigenvalue problem is discussed in many references, among them, Eyring, Walter, Kimball, Quantum Chemistry, Wiley, 1944, Chapter 13.
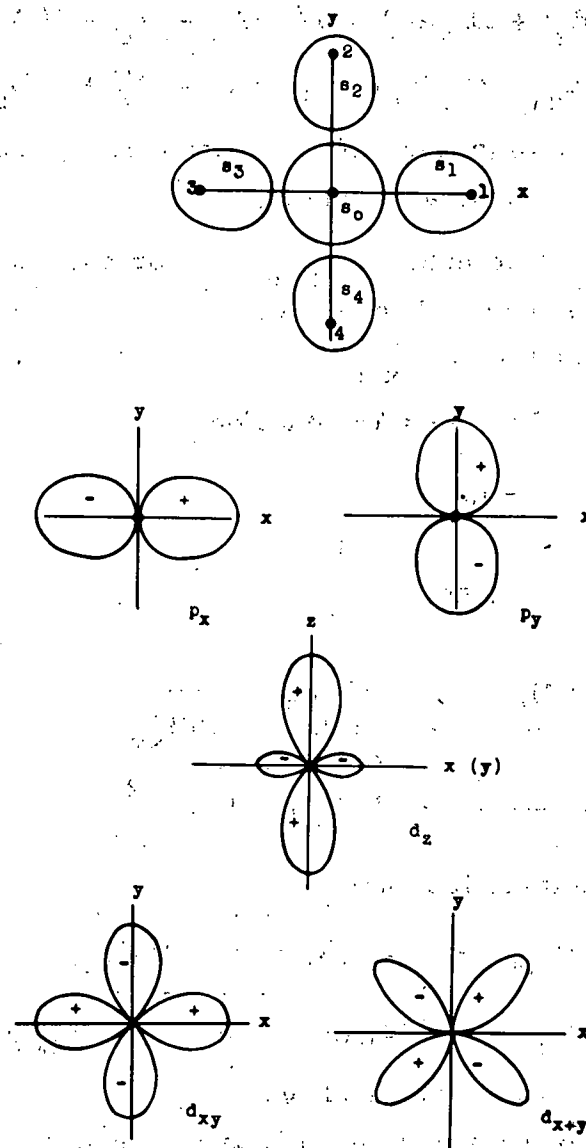
Fig. 32

$$W_3 = \frac{H_s + H}{2} + 1/2\sqrt{A_d^2 + 16B_s^2 + 16B_{dz}^2}$$

Corresponding to these are the eigenfunctions:

$$S_1 = 1/N \left[B_s(d_z) - B_{dz}(s_o)\right]$$

$$X_z = 1/n \left[2B_{dz}(d_z) + 2B_s(s_o) - 1/2(A_d + \sqrt{A_d^2 + 16B_s^2 + 16B_{dz}^2})(S_1)\right]$$

$$X_3 = 1/N \left[2B_{dz}(d_z) + 2B_x(s_o) - 1/2(A_d - \sqrt{A_d^2 + 16B_s^2 + 16B_{dz}^2})(S_1)\right]$$

N is a suitable normalizing factor. X_1 is a nonbonding orbital in our approximation; X_2 is bonding, and X_3 antibonding.

Representation B_1: The orbital, d_{x+y}, is orthogonal to all the other orbitals, and occurs alone here. Therefore,

$$W_4 = H_d, \text{ and } X_4 = d_{x+y}.$$

Representation B_2: The secular equation is

$$\begin{vmatrix} H_d - W & 2B_{dxy} \\ 2B_{dxy} & H - W \end{vmatrix} = 0$$

so that the energies are

$$W_5 = \frac{(H_d + H)}{2} - 1/2\sqrt{A_d^2 + 16B_{xy}^2}$$

$$W_6 = \frac{(H_d + H)}{2} + 1/2\sqrt{A_d^2 + 16B_{xy}^2}$$

The corresponding eigenfunctions are:

$$X_5 = \left[1/N \, 2B_{dxy}(d_{xy}) - 1/2\sqrt{(A_d + A_d^2 \, 16B_{dxy}^2)}(S_2)\right]$$

$$X_6 = \left[1/N \, 2B_{dxy}(d_{xy}) - 1/2\sqrt{(A_d - A_d^2 + 16B_{dxy}^2)}(S_2)\right]$$

X_5 is a bonding orbital, X_6 is antibonding.

The energy levels of representation E are degenerate, and come in pairs. One set is given by the solution of the determinant:

$$\begin{vmatrix} H_p - W & 2^{1/2}B_p \\ 2^{1/2}B_p & H - W \end{vmatrix} = 0$$

The energy eigenvalues are:

$$W_7 = \frac{(H_p + H)}{2} - 1/2\sqrt{A_p^2 + 8B_p^2}$$

$$W_8 = \frac{(H_p + H)}{2} - 1/2\sqrt{A_p^2 + 8B_p^2}$$

where $H_p = p_x \overline{H} p_x$ = etc., $B_p = p_x \overline{H} s_1$ = etc., and $A_p = H_p - H$. A pair of eigenfunctions is:

$$X_{7a} = 1/N \left[2^{1/2} B_p(p_x) - 1/2 \left(A_p + \sqrt{A_p^2 + 8B_p^2} \right)(S_3) \right]$$

$$X_{8a} = 1/N \left[2^{1/2} B_p(p_x) - 1/2 \left(A_p - \sqrt{A_p^2 + 8B_p^2} \right)(S_3) \right]$$

The other pair may be obtained by replacing p_x by p_6, and S_3 by S_4. The X_7 orbitals are bonding, the X_8 antibonding. Our conclusions regarding bonding and antibonding nature of the orbitals depend on the fact that both the H's and the B's are negative quantities; the sign of A does not affect the nature of the orbital, as inspection of the eigenfunctions proves, but affects mainly the splitting between the orbitals.

The orbitals therefore fall into three groups. Four of the orbitals are bonding: $X_2(S_1, s_o, d_z)$, $X_5(S_2, d_{xy}')$, $X_{7a}(S_3, p_x)$ and $X_{7b}(S_4, p_y)$. Two orbitals are essentially nonbonding: $X_1(s_o, d_z)$, and $X_4(d_{x+y})$. Four orbitals are antibonding: $X_3(S_1, s_o, d_z)$, $X_6(S_2 d_{xy})$, $X_{8a}(S_3, p_x)$, and $X_{8b}(S_4, p_y)$. Now zinc porphin complex may be thought composed of a zinc ion and a doubly negatively charged porphin anion. The four nitrogens of the ring bring into the sigma orbital system eight electrons; the 3d orbitals of Zn^{++} are full, so six more electrons in the three d orbitals which are symmetric with respect to the plane are brought into the sigma bonding, the other four being assigned, for the moment at least, to the pi bonding system. Twelve of the fourteen electrons which we must assign may be put into the bonding and nonbonding sigma orbitals. The remaining two must be placed in an antibonding orbital, or be shifted off to the pi electron system. For the sake of continuity, we must anticipate a bit, and assert that similarities of spectra require the former alternative.

We seek next the lowest-energy antibonding orbital in which to put the remaining two electrons. Examination of the expressions for energies of the antibonding orbitals reveals that the energy will increase in the exchange integral B. For zinc ion, the 3d orbitals are filled, the 4s and 4p orbitals empty; in zinc atom, the 4p levels only are empty. This means that H_d is lower than H_s, which, in turn, is lower than H_p. Also, 3 d orbitals are drawn more closely to the zinc ion than would be orbitals of the fourth shell, so we may surmise that their overlap with nitrogen electron orbitals will be comparatively small. These

facts imply that X_6 will be the lowest-energy antibonding orbital, and that its energy will not be very much greater than H_d. The extra two electrons will, therefore, be placed here, and we shall see what are the consequences of this assignment.

We now examine the influence of the metal ion on the pi electron system of porphyrins. The metal provides a pair of d orbitals, d_{y+z} and d_{x+z}, from the third shell, and the p_z orbital from the fourth shell. A molecular orbital calculation for a metal porphyrin complex has not been, and will here not be, carried out, for we do not know well enough the relative values of the parameters H and B of metal and carbon, which are needed for proper placing of the energy levels. We begin, therefore, by displaying the energy level diagram, first computed by Longuet-Higgins, Rector and Platt, for the free-base porphin, [30,43] and then discuss the effect of the metal. Fig. 33 shows the representation of the group D_{4h} to which the level belongs, and the value of the parameter "r" through which the energy is expressed by the formula $W = H + rB$. Free-base porphin has 26 pi electrons: one from each of the twenty carbon atoms, and six from the four nitrogens. These are shown by dots opposite the thirteen lowest energy levels, illustrating the ground electronic state of porphin. Also shown are diagrams indicating the behavior of functions belonging to the different representations under the operation of the group. The letters "g" and "u", as usual, mean even or odd behavior on inversion through the center of symmetry; the orbitals involved are pi orbitals, and hence antisymmetric with respect to the plane of the molecule, accounting for the subscript. Only one of the resolutions of the degenerate set E is shown; an equally good resolution has nodal axes at $45°$ to those shown.

According to Platt, an electron jump from the highest filled A_{2u} orbital to the E_g directly above results from absorption of light of the long-wavelength bands of porphin; the Soret band near $4000Å$ arises from electron jumps from A_{1u} to E_g orbital.**

---

* Notation for the representations is that of Longuet-Higgins, Rector and Platt, and is consistent with that of Margenau and Murphy.

** Platt, et. al., op. cit. , have attributed the Soret band to accidentally degenerate transitions from both the levels A_{1u} and B_{2u} of the same energy level E_g. This degeneracy may indeed be real; it may also be approximate, and removable by better calculations. We have selected A_{1u} only as the origin, since a little consideration shows that this level persists throughout the hydrogenated porphyrin series, as long as the Soret does, and keeps its relative position on the energy-level ladder.

Representation	r
A_{2u}	-2.16
E_g	-2.09
B_{1u}	-2.00
B_{2u}	-1.62
E_g	-1.62
A_{1u}	-1.62
B_{1u}	-0.62
E_g	-0.36
A_{2u}	0.00
A_{1u}	+0.62
E_g	+0.62
B_{2u}	+0.62
A_{2u}	+0.77
E_g	+1.19
B_{1u}	+1.62
B_{2u}	+2.00
E_g	+2.26
A_{2u}	+2.39
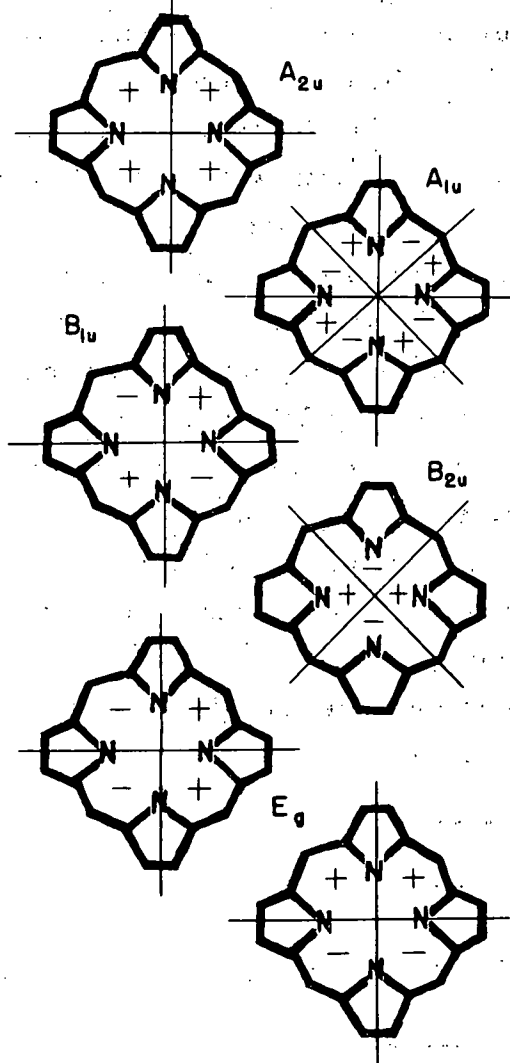
Fig. 33

Inspection of the metal orbitals shows that the p_z orbital is of representation A_{2u}, and the d orbitals are of representation E. Therefore if we put a metal ion in the center of the ring, we will find a new A_{2u} energy level and a new degenerate pair of E energy levels. The other representation will be unchanged in energy values and in the number of orbitals. If there were no overlap between the metal orbitals and the ring orbitals, the new levels would simply have energies H_p and H_d. We know that H_p is higher than H_d, and since we have four electrons to hide somewhere, in the case of zinc, we place the new E level, (E_d), below the highest filled A_{2u} level, and the new $A_{2u}(p_z)$ level somehwere above the E_g level. The highest filled orbital will still be the old A_{2u}. Any other arrangement of orbitals and electrons, or any attempt to transfer the two electrons assigned to orbital X_6, can be shown to result in the appearance of permitted transitions in the spectrum of zinc porphin which persist in copper porphin but disappear in nickel porphin. Overlap between the metal and the ring orbitals will change the energy values, but in a way which is not easily determinable. In the case of the p_z metal orbital, at least, overlap is probably almost negligible, due to the spatial distributions of this and the nitrogen orbitals.

This argument, which is completely ad hoc, will be used to correlate and-- we hope-- clarify a little the spectra and other physical properties of the metal porphyrin complexes.

Let us diagram the state of affairs we propose for zinc porphin.

Pi Orbitals		Sigma Orbitals
$A(p_z)$ ____		
E_g ____		
		X_6 ____
		X_1 ____
A_{2u} ____		X_4 ____
$E(d)$ ____		
A_{1u} ____		X_5 ____

It is true that transitions between sigma and pi states are permitted, for terms of proper symmetry, but only by the dipole matrix element in the direction perpendicular to the plane of the molecule, and since this element is small, such transitions are probably weak and would easily be obscured by the strong pi electron transitions.

Before proceeding through the transition elements, let us see what happens in the case of magnesium porphyrin. Here there are no low-energy d orbitals; the eigenfunction for X_5 shows that it has become a nonbonding orbital, S_2, composed entirely of nitrogen orbitals. The other orbitals derived from d orbitals, X_1, X_4, X_6, and $E(d)$, have disappeared, or rather risen to inaccessibly high energy values. The orbital $A(p_z)$ is still present, but probably of high energy. The diagram of the situation in the vicinity of the states involved in transitions is now quite simple:

Pi Orbitals   Sigma Orbitals

$A(p_z)$ ____

E_g ____

A_{2u} __ __ S_2 _____

A_{1u} __ __

As we proceed from zinc down through the transition metals, two salient changes occur; the number of electrons in the system decreases, and the energy of an electron in a 3d orbital (H_d) increases, owing to smaller nuclear charge. The perseverance of the spectrum throughout the transition group indicates that as we go down through that group, electrons are removed from the sigma states involving d orbitals, or, in effect, from the d orbitals of the metal ion, thus leaving the pi system unchanged. In our diagram of zinc porphin, the highest filled level is X_6. Copper porphin will therefore have only one electron in this level. Nickel porphin has none in this level, and we diagram the state of affairs thus, where the nonbonding orbitals have been raised in response to increase of energy of d orbitals.

Pi Orbitals   Sigma Orbitals

$A(p_z)$ ____

E_g ____

                                     X_6 _____
                                     X_1 _____
                                     X_4 _____

A_{2u} _____

$E(d)$ ......

A_{1u} _____ X_5 _____

We are now able to offer a little experimental justification for our ordering of the energy levels. It is well established that nickel porphyrin complexes are diamagnetic;[18] since this complex has two less electrons than the zinc complex, which is also diamagnetic, the highest filled level in zinc porphin must be non-degenerate, ruling out E_g, $E(d)$, X_8 and the practically degenerate pair X_1 and X_4, and leaving X_6 as the only candidate. Similarity of the spectra of the zinc and nickel complexes rules out $A(p_z)$.

We also now have a possible explanation for the lack of fluorescence and phosphorescence of the transition group complexes, depending upon the presence of empty sigma levels between the ground and excited level or porphins. Excitation ($A_{2u} \longrightarrow E_g$) is followed by the forbidden transition ($E_g \longrightarrow X_6$), and then by permitted decay from that level to the ground state ($X_6 \longrightarrow A_{2u}$). It may be that these porphins fluoresce in the infrared, and that this has not yet been observed. A case similar to this has been reported for europium complexes of salicylaldehyde.[47] Reduction of nickel porphin is about as slow as that of copper porphin, indicating lack of high-energy long-lived triplet or quartet states in both of these.

After nickel, electrons will be lost from the nonbonding orbitals X_1 and X_4. For ferrous porphin:

Pi Orbitals

$A(p_z)$ _____

E_g _____

A_{2u} _____

$E(d)$ ....

E_{1u} _____

Sigma Orbitals

X_6 _____
X_1 _____
X_4 _____

X_5 _____

On reaching chromous porphin, the nonbonding orbitals are empty.

Pi Orbitals

$A(p_z)$ _____

E_g _____

$E(d)$ ....

A_{2u} _____

Sigma Orbitals

X_6 _____

X_1, X_4 _____

X_5 _____

Vanadous and titanous porphins would have to lack electrons in the degenerate $E(d)$ orbitals, which by now consist mainly of the d_{x+z} and d_{y+z} orbitals. These compounds, which have not yet been prepared, should have interesting spectral and electromagnetic properties. If we lose enough electrons,

we reach calcium porphin, which has the same configuration as magnesium porphin, and the spectrum returns to normal.

Most of the known porphin complexes can be accommodated to the description just given quite easily, necessary changes being made of the orbitals involved. In conclusion, let us apply this picture to the question of bond strength between metal and porphin ring.

The relative lability of the metal in porphin complexes has been studied.[3] Some metals, such as magnesium, are weakly held to the ring, and are released by mild agents such as water. Others, like zinc, require acid of some strength to release them. Still others, like nickel and copper, cannot be released without decomposition of the ring. Inspection of the orbitals shows that magnesium is held to porphin by three bonding orbitals, X_2, X_{7a}, and X_{7b}, since X_5 is nonbonding here, or is bonded to each nitrogen by three-fourths of a bond. In zinc porphin, there are four bonding sigma orbitals, including X_5, and two bonding pi orbitals, $E(d)$, but one antibonding sigma orbital, X_6, which acts to weaken the bond. In nickel porphin this antibonding orbital is no longer occupied, effectively increasing by one the number of bonds holding metal to nitrogens. This, we believe, explains the looser bonding of zinc porphin, and the absence of bonding pi orbitals explains the still greater lability of magnesium in its porphin complex.

We shall find it convenient soon to argue sometimes with the free-base porphyrin, sometimes with a metal complex; the purpose of the preceding section is to assure us that any conclusions about spectra reached by use of the free base will be valid also for the metal complexes, and vice versa.

Structure of Bacteriochlorophyll

It has been known for years that bacteriochlorophyll is a tetrahydroporphin, but until very recently it and its derivatives have stood alone in its class, since none had been synthesized, and reductions of chlorophyll had apparently not yielded bacteriochlorophyll derivatives.[45] Recently, however, Dorough has reported the isolation of not one but two tetrahydroporphins, by catalytic hydrogenation of tetraphenylchlorin free base.[12] His yields are small (2 to 4 percent), but he has been able to verify their stage of hydrogenation. One of the compounds, which he calls "Alpha", has a spectrum unmistakably similar to that of bacteriochlorophyll, with its intense band near 8000Å, and a weaker band in the green. The other compound, "Beta", is the same as the tetrahydroporphin described in this thesis, as shown by the identity of the spectra, both of the free

base and of the zinc complex. Both of these tetrahydroporphins form metal complexes, and both are oxidized by quinone to porphin, and so are similar in known chemical properties. Dorough reports, however, that "Alpha" is less prone to form metal complexes.

The difference between these two compounds must lie in the placement of the four "extra" hydrogens, and, in fact-- since both compounds arise by reduction of chlorin-- in the placement of the two additional hydrogens. The only places where hydrogens may be added to chlorin, and not break the all-important conjugation of the great ring, are the beta positions of the pyrrole rings. We come therefore to the conclusion that one tetrahydroporphin has adjacent pyrrole rings hydrogenated, and the other has opposite pyrrole rings reduced. The former will be called I, II-tetrahydroporphin, the latter, I,III-tetrahydroporphin.
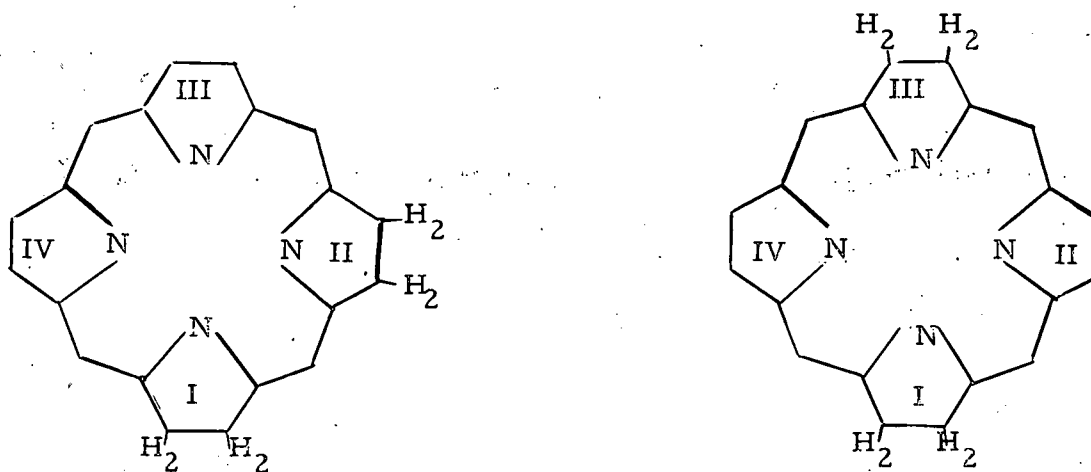
We shall try to decide which form represents "Alpha" and which "Beta".

The generally accepted structure for bacteriochlorophyll is of the I, III type. Because of similarity of the spectra, Dorough has assigned to compound Alpha the same structure, and leaves open the question of the structure of Beta, although suggesting that it may be of the I, II type. Platt, also assuming that bacteriochlorophyll has the I, III skeleton, presents a rationalization of its spectrum by considering the effect of perturbations on oscillator strengths of even-odd transitions.[36] He presents his argument only tentatively, for, since the perturbations involve tampering with the resonating system itself, it requires an extreme extension of his general theory. Worse, he was not aware of the existence of the Beta-type compound, with its spectrum so like that of porphin; his treatment would seem to predict that both Alpha and Beta should show absorption in the red, beyond the chlorin absorption, for the effect of the extra hydrogens should be additive in both cases, showing the first absorption band toward the infrared. His argument, therefore, does not seem

capable of distinguishing between the two forms.

Dorough's characterization of Alpha as I, III-tetrahydroporphin rests entirely upon its resemblance to bacteriochlorophyll, reputed to be the I, III isomer.[37] The structure of bacteriochlorophyll has been reviewed recently,[46] and it appears that the only evidence of I, III reduction comes from the work of Mittenzwei.[32] He, studying the results of chromic acid oxidation of bacteriochlorophyll derivatives, could isolate from the reaction mixture only hemotricarboxylic imide,

$$CH_3-C(H)-C(H)-CH_2CH_2COOH$$ with $$C=O, C=O, N-H$$ (imide ring)
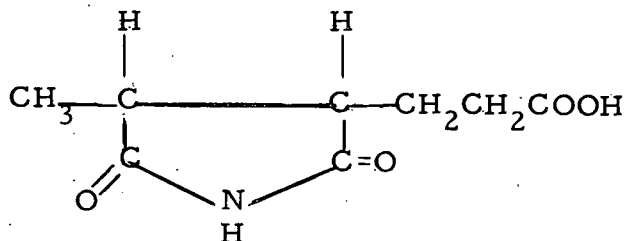
and a small quantity of oil eventually identified as methyl ethyl succinic anhydride,

$$CH_3-C(H)-C(H)-CH_2CH_3$$ with anhydride ring ($C=O, O, C=O$)
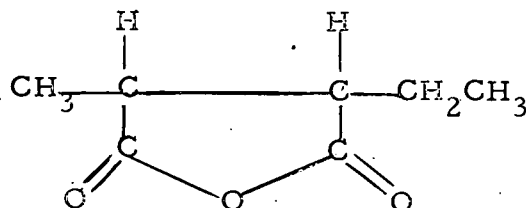
On the basis of this, he proposed the following structure for bacteriochlorophyll. The positions of the side groups were not in question in his researches; only the positions of the hydrogens. It is evident that the hemotricarboxylic
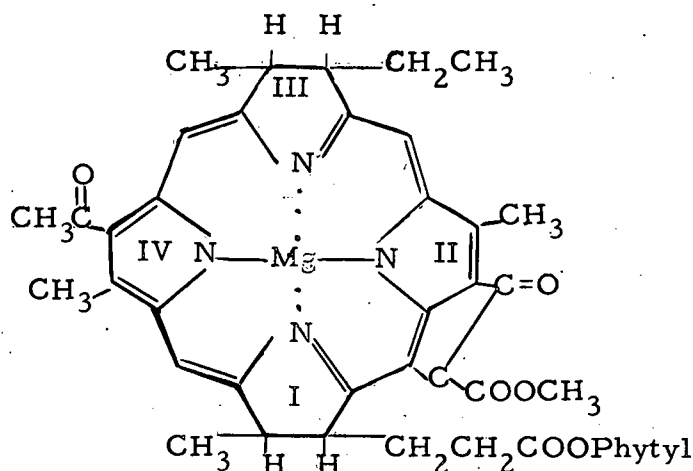
imide could only have come from pyrrole I, but Mittenzwei also asserts that the methyl ethyl succinic anhydride could only come from pyrrole III, there-fore establishing the other hydrogens there. No peculiar derivatives from pyrroles II and IV were found, or even expected, owing to activating influence of the carbonyls during the degradation. Now the odd thing about this is that examination of the proposed structure shows no reason why ring I should be pre-served through the oxidation and emerge as an imide, as is normal in degrada-tions of chlorophyll derivatives, whereas ring III should be hydrolyzed to the anhydride, and in poor yield at that. No imide was ever obtained from ring III in degradations of four different bacteriochlorophyll derivatives. It would seem more likely that under the severe conditions of the oxidation some of ring I is hydrolyzed and decarboxylated to yield a small amount of the succinic anhydride, and that, for some reason, ring III was altogether consumed. Mittenzwei apparently did not consider this possibility, for he makes no attempt to refute it. The only controls run were on chlorophyll derivatives similar to those of bacteriochlorophyll, and although then no anhydride is found, we ought not to expect the chemistry of chlorophyll and bacteriochlorophyll to be any more similar than their spectra. In view of absence of adequate controls (which would have to consist of degradations of tetrahydroporphins of known structure), we must admit that the question of skeletal structure of bacteriochlorophyll, and hence of compound Alpha, remains completely open. Further, Mittenzwei speaks frequently of the lability of two of the hydrogens, which are oxidized off upon slight provocation, leaving chlorophyll derivatives. It would be harder to explain the special lability of hydrogens on ring III than if they were on rings II or IV, under the activating influence of the carbonyl groups.

When our tetrahydroporhin was first found, and its spectrum first known, we were struck by the great similarity to the spectrum of porphin. The absorp-tion bands of the two compounds almost coincide in position; only relative inten-sities were different. The spectra are, if anything, more similar to each other than either is to chlorin. When the hexahydroporphin was discovered, its band system in the red appeared rather more like that of chlorin than like either tetrahydroporphin or porphin.

Now the symmetry group of porphin is D_4. Hydrogenating it to the chlorin reduces the group to C_2, and occasions a change in the spectrum. But further hydrogenation to I, III-tetrahydroporphin partially restores the symmetry to the group D_2. It seemed intuitively apparent that we should also expect a par-tial restoration of the spectrum toward that of porphin, and since our compound

Beta shows such restoration, it appeared to merit characterization as I, III
tetrahydroporphin. By way of contrast, I, II tetrahydroporphin is still of group
C_2, but with respect to a different axis from chlorin, and might well be expected
to show chlorin characteristics to an exaggerated degree, perhaps fitting com-
pound Alpha. We shall now attempt to give further support to this hypothesis
and then turn the chemical evidence at our disposal to its support.

We first wish to establish an obvious but important fact: chlorins, I, II
tetrahydroporphins, and hexahydroporphins have dipole moments, whereas
I, III tetrahydroporphins have only a quadripole moment. We shall illustrate
this first using "classical" valence-bond resonance structures, then interpret
the result in electrostatic terms, and show that it is what we would expect. The
number of simple resonance structures that could be drawn for any porphyrin is
impossibly immense; we shall confine ourselves to structures where only the
nitrogens bear charges. This will be satisfactory, for the carbon atoms in the
beta position of the pyrrole ring in which we are chiefly interested are in allylic
resonance with the nitrogen of the ring, and so should share its charge. We
put further into the center of the ring a metal such as magnesium, which we
may require to form only linear, sp hybrid bonds, and not right-angled bonds.
Magnesium normally forms such linear bonds, and not right-angled ones, so
we are not at all restricting the usual rules for formulation of resonance struc-
tures. On the following pages are drawn all resonance structures, subject to
the above conditions, for chlorin, I, II tetrahydroporphin, I, III tetrahydropor-
phin, and hexahydroporphin, having zero, one, and two charge separations.
No resonance structures subject to the above conditions can be drawn for octa-
hydroporphin, made by hydrogenating all beta pyrrole positions. This probably
accounts for lack of discovery of such a compound by means of bands in the
visible. In order to save drawing, we indicate by a number in parentheses
next to a figure the number of resonance forms having the same charge distri-
bution and metal-bond direction, but differing only in the location of double
bonds around the great ring.

Looking first at the resonance forms involving no charge separation, we
see that for I, II tetrahydroporphin and hexahydroporphin the only forms that
can be drawn require fixed bonds, while for chlorin and I, III tetrahydropor-
phin uncharged structures can be drawn involving mobile double bonds. Since
the difference in energy between forms with fixed and with mobile bonds is
roughly the resonance energy of an eighteen-membered conjugated ring, this
suggests that the contribution of uncharged resonance forms to the ground

electronic state will be rather greater for chlorin and I, III tetrahydroporphin than for the other two.

Construction requires that the dipole moment arise from contributions from resonance structures involving single charge separation. Because of symmetry, I, III tetrahydroporphin, like porphin itself, has no dipole moment. For the other three compounds, we might compare their dipole moments by finding the average charge on each nitrogen over all resonance forms with single charge separation. If we do this, we find the distribution:
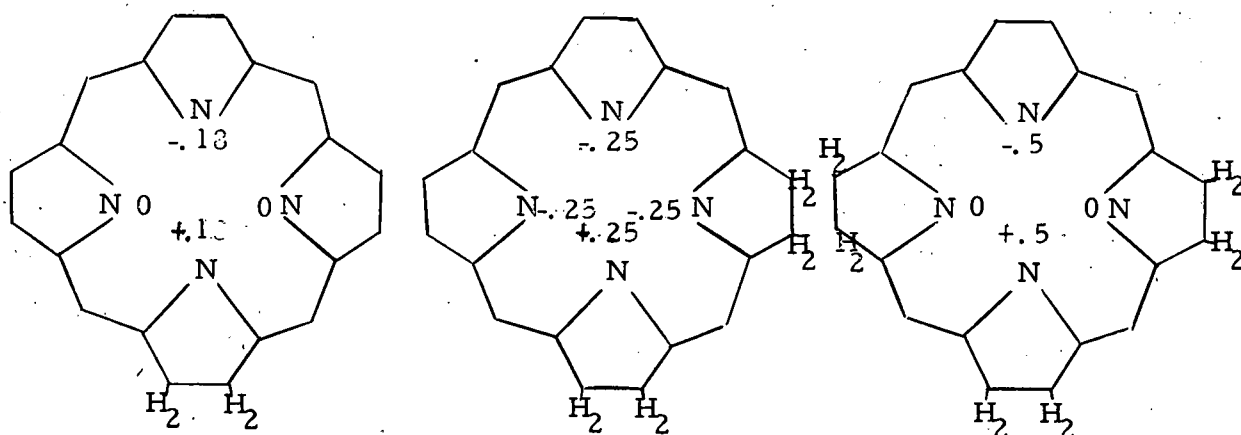
For chlorin, we find a charge separation of 0.18 for I, II tetrahydroporphin and hexahydroporphin, 0.5. As intimated before, the presence of unchanged forms for the chlorin, with mobile double bonds, will minimize the contribution of polar structures to the ground electronic state, leaving chlorin with only a small dipole moment. But the only forms of I, II tetrahydroporphin in which the double bonds are not fixed are precisely those with single charge separation, which contributes most to the dipole moment. We should therefore expect the ground state of this compound to be strongly dipolar, with its moment vector oriented at 45° to that of chlorin. This result would not be changed if we took explicit account of the sixteen resonance structures which have metal bonds at right angles. With hexahydroporphin, no structures have been drawn with mobile bonds, so there is not much preference. The uncharged structure is probably predominant, leaving hexhydroporphin with a dipole
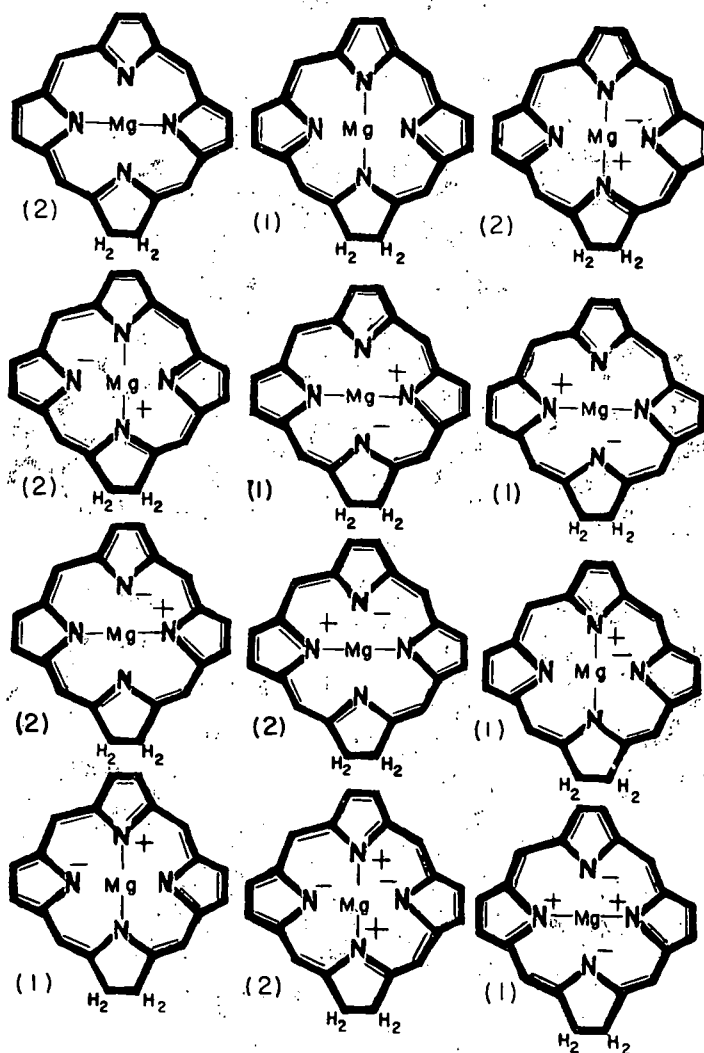
CHLORIN

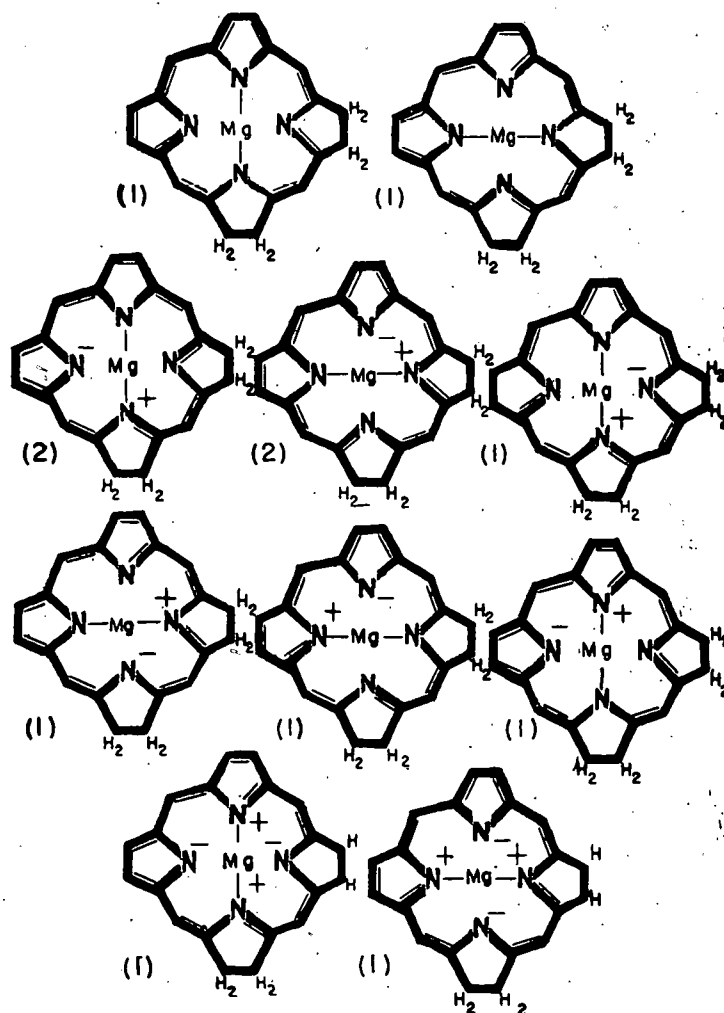
Fig. 34

I,II TETRAHYDROPORPHIN
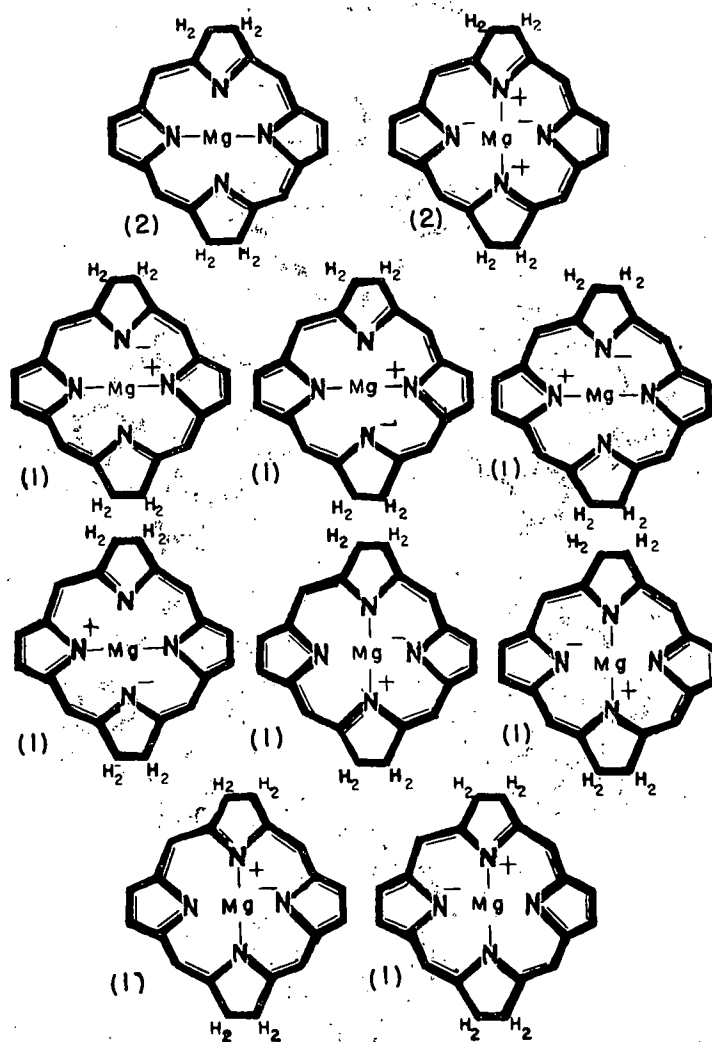

Fig. 35

I, III TETRAHYDROPORPHIN
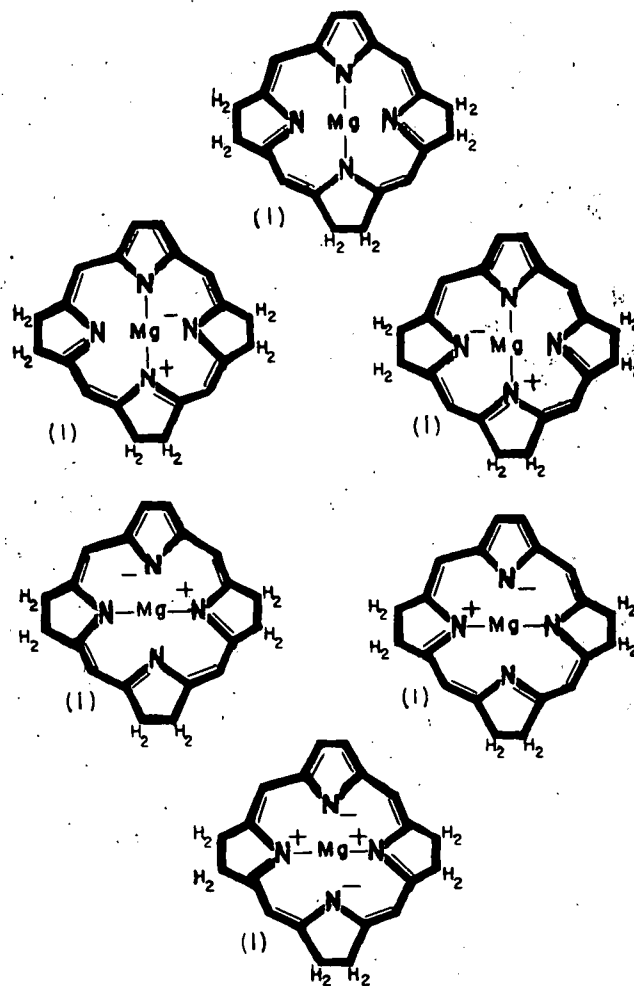

Fig. 36

HEXAHYDROPORPHIN

Fig. 37

moment somewhat larger than that of chlorin.

Inspection of the forms with two charge separations shows that chlorin, I, III tetrahydroporphin, and hexahydroporphin have quadripole moments; I, II tetrahydroporphin does not. These forms should make no great contribution to the ground states.

This discussion has been from the point of view of valence bond theory. In electrostatic terms, the results mean that the metal ion in the center of the ring attracts electrons from the four nitrogens impartially, but those nitrogens on hydrogenated pyrrole rings are not as capable of making up the electron deficit by drawing in electrons from the hinterland as the nitrogens on unreduced pyrrole rings, and so are positively charged relative to these latter nitrogens. Precisely the same argument holds when protons are in the center of the ring, so we may expect the free bases to show about the same dipole and quadripole moments as the metal salts.

We have, by these arguments, in particular established that I, II tetrahydroporphins should have rather large dipole moments, and I, III tetrahydroporphins only small quadripole moments.

An important and well-known relationship between the color of compounds and their constitution is that compounds in which the conjugated system supports a charge separation, hence usually a dipole moment, are more deeply colored than similar compounds without charge separation.[16] Advantage is taken of this in dyeing by the use of auxochromes, which are essentially electron-rich groups that feed their electrons to relatively electron-deficient chromophores. Many compounds owe their deep color to this fact, such as
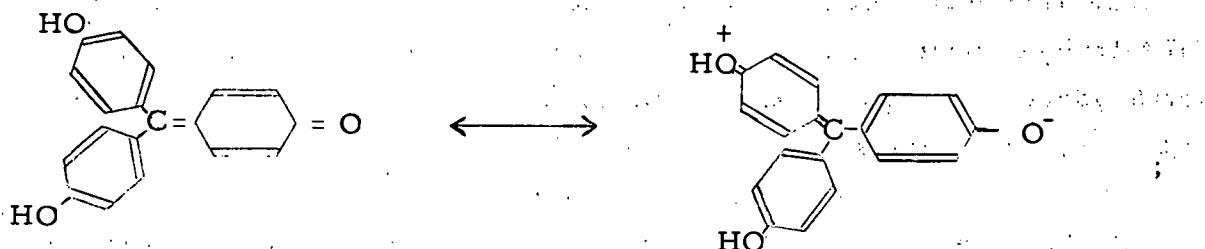
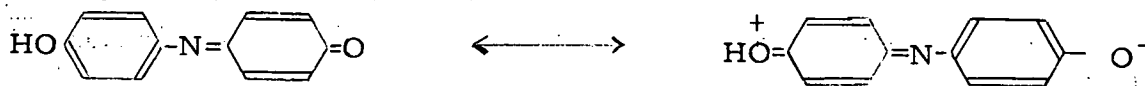p-nitro-p'-dimethylamino-azobenzene,
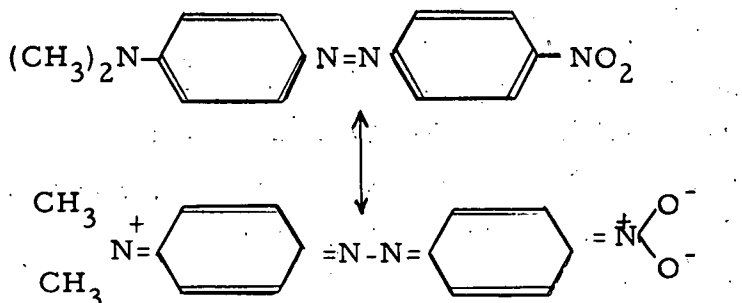
quinoline yellow,
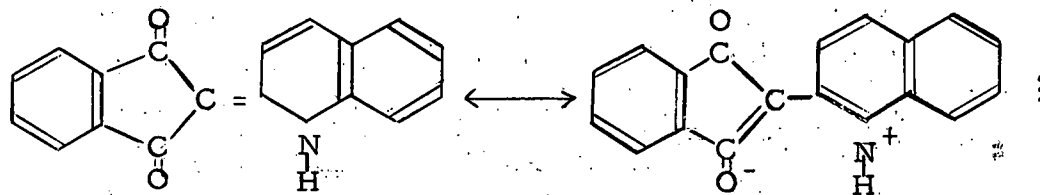
aurin,

and phenolindophenol,

We have in I, II tetrahydroporphin another such compound, one with unusually strong charge separation, and should expect this to produce a "deepening of color", that is, move the absorption band over toward the infrared. Compound Alpha fits this description much better than compound Beta. The small quadri-pole moment of I, III tetrahydroporphin must account for the appearance of the spectrum of compound Beta, where the splitting of porphin's degenerate orbital E_g is less than in the dipolar chlorin.[*]

Again, from the structure, we would expect the I, III tetrahydroporphin, like the porphin, to show a typical "round field" spectrum, with weak first and strong second transitions, which is the case with Beta. I, II tetrahydroporphin should, from its structure -- geometrical and electrical -- approximate the "long field" type, with strongest first transition, and Alpha shows this characteristic.

We have by now presented two reasons for preferring the I, II structures for compound Alpha and the I, III structure for compound Beta: the I, III tetra-hydroporphin structure for bacteriochlorophyll does not explain satisfactorily the lability of its hydrogens, or its oxidation products; the spectra of the com-pounds fit our assignment better. Four other pieces of evidence will now be offered in support.

Hexahydroporphin, shown here in one of its resonance forms, is oxidized rapidly and cleanly in the dark by oxygen to give the Beta tetrahydroporphin. As we have shown, ring II bears the most positive charge, so the hydrogens thereon should be most easily removed by electronegative oxygen molecules. If this is done, I, III tetrahydroporphin results.

[*]   The degeneracy of porphin's first transition is well known, having been
      inferred from studies of spectra of substituted porphyrins. Cf. (3), and (29).
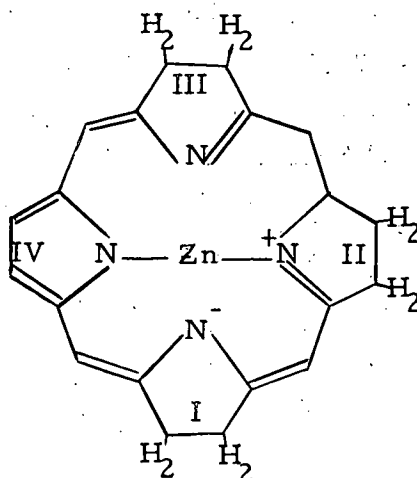
We do not know whether benzoin in its triplet excited state acts to reduce zinc chlorin by first transferring protons or electrons. As we have shown, the dipole of chlorin puts strongest negative charge on ring III, and the quadripole moment puts small negative charges on rings II and IV.
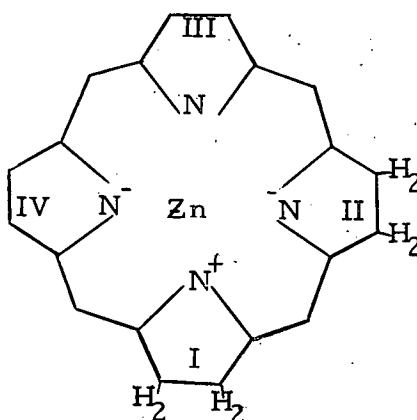
If benzoin transfers protons first, they should go onto the more highly negative ring III, forming I, III tetrahydroporphin, which is actually Beta. If, however, electrons were transferred first, we should expect chlorin to be reduced more slowly than porphin, because its susceptible spots are relatively negatively charged. The steady-state concentration of chlorin is usually quite small, indicating that it is reduced more rapidly than porphin, making proton transfer the more likely mechanism, and affirming that Beta is the I, III tetrahydroporphin.

Quinones oxidize zinc tetrahydroporphin (Beta) much more slowly than they do zinc chlorin. Although here the porphyrin is reacting in its triplet excited state, the fact that in the ground-state I, III tetrahydroporphin the rings bearing extra hydrogens are considerably less positively charged than the hydrogenated ring of chlorin may contribute to the slower oxidation of the former. Since the hydrogenated pyrrole rings of the ground state of I, II tetra-

hydroporphin are highly positively charged, one would expect that compound to be oxidized about as rapidly as chlorin. Dorough has not yet published quantum yields on the oxidation of Alpha, although he reports that it takes place.

Finally, Dorough and Shen have attributed changes in absorption spectra of free-base porphyrins at low temperatures to isomerization among the N-H bonds in the center of the ring.[8] They report that Beta shows the same type of behavior as to porphin and chlorin, but Alpha shows no change of this type. Considering the charge distribution on the nitrogens of the two tetrahydroporphins, it is apparent that in the I, II isomer the hydrogens should be quite firmly attached to the two negative nitrogens, but that in the I, III isomer, with its weakly charged nitrogens, the hydrogens should be free to isomerize. We therefore expect the spectrum of the I, II isomer to show little temperature variation from the above cause, while the I, II isomer should behave like porphin and chlorin. This further identifies Alpha as the I, II isomer, and Beta as the I, III isomer.

One last problem remains unsolved. If the extra two hydrogens are not located on ring III of bacteriochlorophyll, are they located on ring II or on ring IV? For light on this subject, we again turn to the work of Mittenzwei.[32]

He reports a series of reactions, in which the acetyl on ring IV is reduced by the Meerwein-Ponndorf method to the alcohol, and this at upwards of $200°$ splits off water to give a vinyl bacteriochlorophyll. If the extra hydrogens were
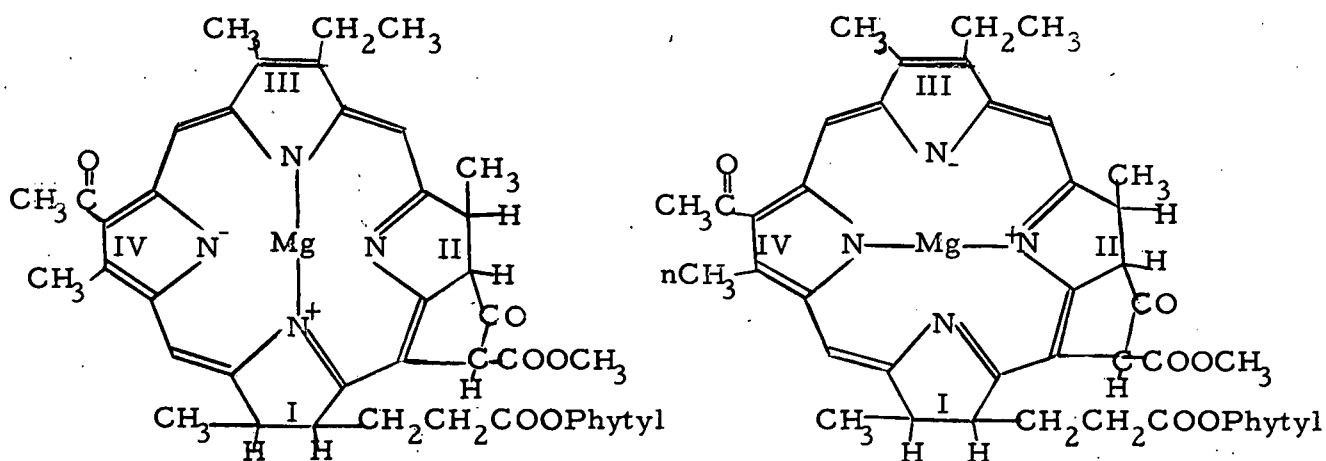

Bacteriochlorophyll
(Mittenzwei)
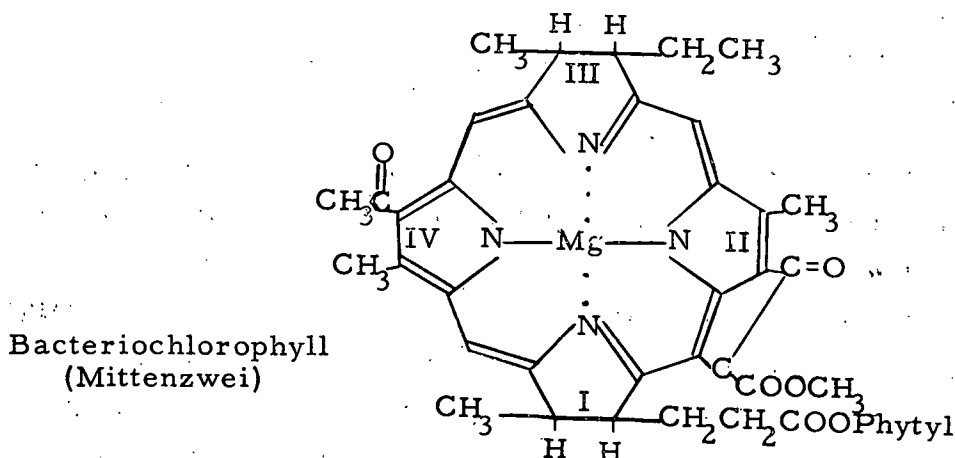
on this ring, it would seem certain that dehydration would go in such a manner as to bring the double bond into conjugation with the ring, forming an ethyl chlorophyll, perhaps, instead of the vinyl bacteriochlorophyll actually obtained as evidenced by the spectrum. This is quite good evidence that the hydrogens are not on ring IV, and the only place left is ring II.

As positive evidence for this may be cited Mittenzwei's experience that cycliza-
tion of bacteriochlorin e_6 trimethyl ester to bacterio-methyl pheophorbid a
is difficult, because of extreme lability of the extra hydrogens, indicating
they may be near by on ring II.
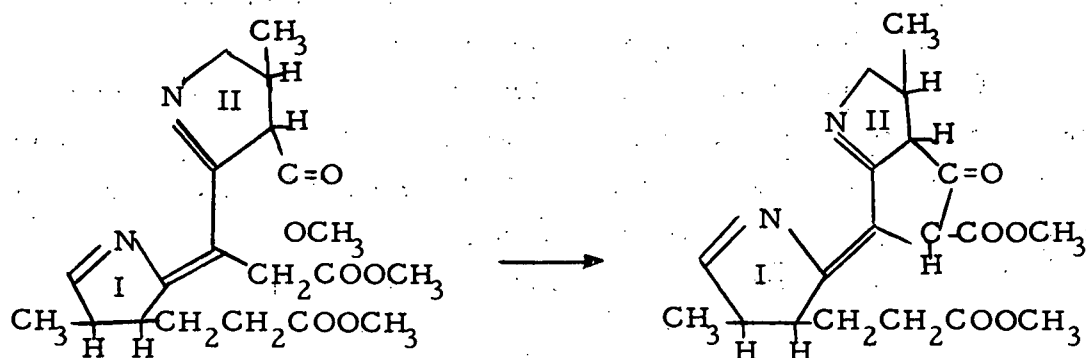
We therefore propose the following structure for bacteriochlorophyll, as
being the most consistent with all the experimental evidence. A final remark:
remembering that the chromic acid degradation takes place in strongly acid
solution, we realize that the negative charge accumulated on ring III may make
it unusually susceptible to attack, and account for its destruction.

Bacteriochlorophyll

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6 - 120