equilibrium oxygen pressure in atmospheres into the formula $\Delta F^0 = +RT \ln P_{O_2}$. The value of the pressure in each case was chosen to fall on the linear portion of the equilibrium curve. The value of $\Delta H - \Delta F^0/T$ listed in line four is then approximately equal to the ΔS of the oxygenation.

The ΔH values, calculated from the oxygen pressures at 0 and 25° are 15,000 cal. for CoSaEn and 7,200 cal. for 3-EtO-CoSaEn. The agreement is not too bad for the CoSaEn and the large deviation, in the case of the 3-EtO-CoSaEn, is not expected since these data are less accurate than any of the other measurements. The discrepancy in both cases is believed to be due largely to a lack of attainment of equilibrium in the 0° measurements. This is confirmed by a calculation of the ΔH values from the 25° and the single point at 40° for CoSaEn and at 50° for the 3-EtO-CoSaEn. ΔH values of 19,200 cal. and 19,300 cal., respectively, are obtained in good agreement with the measured heats.

These are, of course, crude calculations but they are sufficient to illustrate the general nature of the oxygenation process. It is apparent that the small change in free energy and appreciable oxygen pressures are a result of the rather large heat and entropy effects cancelling each other. The entropy loss of 50–60 entropy units is somewhat more than the translational entropy of oxygen gas and is even greater than the total molal entropy of oxygen at 25° (40.3 e.u.). However, this loss of translational entropy is probably the most important factor in the large entropy change.

Summary

The oxygen equilibrium pressures over four crystalline oxygen-carrying chelates have been measured as a function of the degree of oxygenation. The X-ray powder diagrams of one of these compounds have been followed through the range of composition from 0 to 92% oxygenation. It has been demonstrated by both methods on at least one compound that this is not a simple three phase system (gas and two solid phases) but also involves at least one region of solid solution.

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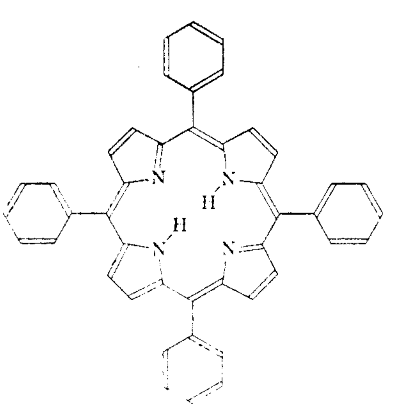
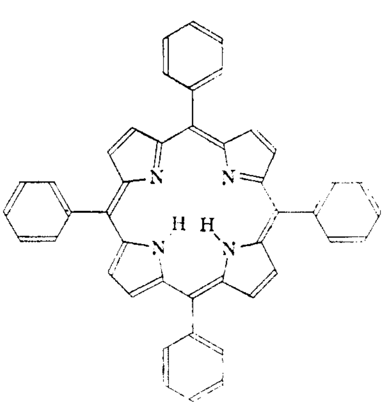
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

A Further Study of the Porphine-like Products of the Reaction of Benzaldehyde and Pyrrole

BY RUSSELL H. BALL,[1] G. D. DOROUGH AND M. CALVIN

It has been observed[2] that the rather general reaction of aldehydes with pyrrole to give methine carbon substituted porphines many times yields two porphine-like products which are separable by acid fractionation or chromatography. Rothemund has proposed[2] that these two products are examples of isomers of the type





Only in the case ~~of~~ porphine itself, however, were the two forms isolated and analyzed; in all other cases, the isomerism was inferred from differences in absorption spectra and basicity. The suggestion that these differences are due to an isomerism of the above type meets with several strenuous objections, the most important of which is the fact that the two compounds upon complexing with a metal such as copper yield different rather than identical porphine salts.

It is the purpose of this paper to demonstrate conclusively that in one case at least, that of the reaction of benzaldehyde with pyrrole, the two main porphine-like products formed are not isomeric. As in previous papers[3,4] we shall refer to these products by the letters A and B. Occurring in the largest amount is material A, which has a spectrum characteristic of etioporphyrins (see Fig. 1), and an HCl number of 13.5. In lesser amounts is material B, which has a spectrum unlike any known por-

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[1] Abstracted in part from the thesis presented by Russell H. Ball to the University of California, 1945, for the M.S. degree.

[2] Rothemund, THIS JOURNAL, **61**, 2912 (1939); **63**, 267 (1941).

[3] Aronoff and Calvin, *J. Org. Chem.*, **8**, 205 (1943).

[4] Calvin, Ball and Aronoff, THIS JOURNAL, **65**, 2259 (1943).

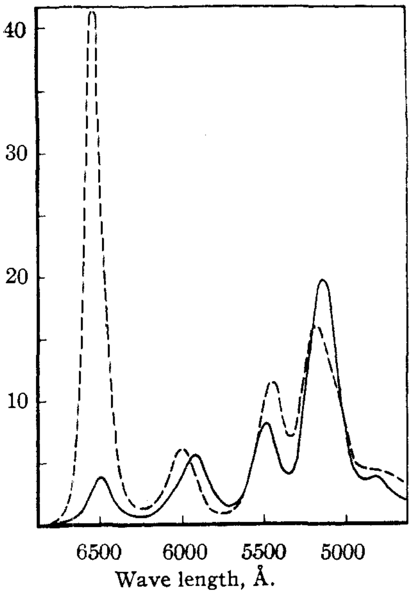

Fig. 1.—Free base spectra: solid line, component A, dotted line, component B.

phyrin (see Fig. 1), and an HCl number of 19.5.[5]

Since the spectra of chlorins are characterized by an intense absorption band in the red, the suggestion was made[4,6] that material B might be a chlorin rather than a porphine. Chlorins are porphines with one reduced pyrrole nucleus, *i.e.*, dihydro porphines. Calvin, Ball and Aronoff[4] gave added weight to this suggestion by establishing in a set of preliminary experiments an oxidation–reduction relationship between the two compounds. These preliminary experiments have now been expanded and made more quantitative, and they bear out in full the conclusions which were drawn in the preliminary work. In addition, sufficiently large amounts of the two compounds have been isolated to permit direct analysis, and the result of this, too, is in agreement with non-isomeric structures for A and B.

Experimental

Preparation of Material.—The free base material is synthesized by heating in a closed bomb tube 5 cc. of pyrrole and 10 cc. each of benzaldehyde and pyridine.[3] It has been observed that the amount of B relative to A is increased by running the reaction at higher temperatures—thus, the product of the reaction at 170° contains about 4% B, that at 200° about 12% B, and that at 220°, 20 to 25% B. For experiments requiring large amounts of only fairly pure A, product from 170° runs can be used as it comes from the reaction mixture.

It was discovered in the course of this work that the yield of porphine material could be greatly increased by the addition of 5 g. of zinc acetate to the reaction mixture. Thus yields of 10–11% (based on pyrrole) were obtained from the reaction with zinc acetate, as against yields of only 4 to 5% for the usual free base run. The product in the former case is the zinc complex of the porphine material. Since the action of 6 *N* hydrochloric acid will readily remove the zinc from the porphine ring, the conversion of the zinc complex to the free base is a simple matter. The composition of free base derived in this manner from the directly synthesized zinc complex does not show the temperature dependence characteristic of the free base prepared directly, but consists in all cases of practically pure A.

For the preparation of large amounts of A material, either Zn complex or free base, this latter method is obviously well suited, and was employed as such.

Separation of A and B.—In order to effect a separation of the products of the reaction, the crystalline material isolated from a high temperature synthesis is dissolved in trichloroethylene and chromatographed on talc. Our experiments have shown that the limiting amount of material which can conveniently be chromatographed on a column of 12 to 16 inches in length is approximately 9 mg. of porphine per square centimeter of cross-sectional area of the column. On the developed column, material A appears at the bottom as a grassy green layer; material B appears immediately above the A material as a brownish green layer. The layers are mechanically separated and eluted individually in the following manner: The porphine-containing talc is repacked in a column of appropriate size and the eluent (pyridine) is drawn through the column in the same manner the original column was developed. Practically quantitative recovery is effected by this means. To obtain samples of high purity the materials from the individual layers must be rechromatographed.

Oxidation of the Copper Salt of B.—About 1 mg. of B free base was dissolved in 10 cc. of glacial acetic acid. The solution was boiled for a few minutes to expel air, an excess of copper acetate and sodium acetate were added, and the boiling continued for a few additional minutes to form the copper complex. This complex-containing solution was diluted rapidly with air-free water, extracted with ether, the ether solution washed with 25% hydrochloric acid until free of unreacted base, dried, and the absorption maxima measured at 6150 and at 5380 Å., respectively. The ratio of these maxima was 1.16 (6150/5380) (see Fig. 2).

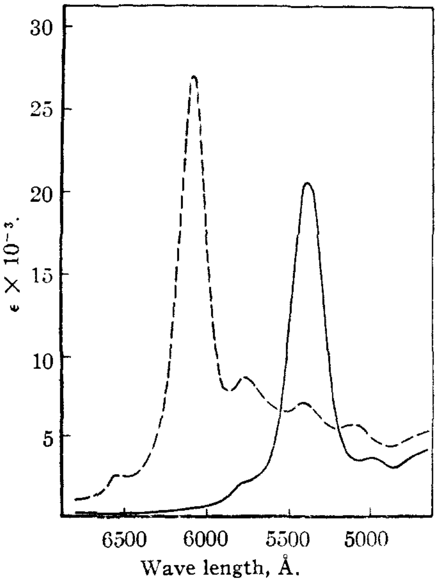

Fig. 2.—Copper complex salts: solid line, component A, dotted line, component B.

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[5] Although this is not true of his earlier publications, the latest report of Rothemund given before the Cleveland meeting of the Organic Division of the American Chemical Society, April 1944 (page 42M in the Abstracts of Papers), cites HCl numbers and positions of first absorption maxima for his tetraphenyl porphine and tetraphenyl isoporphine which are in agreement with the values given above for A and B, respectively.

[6] Pruckner, *Z. physik. Chem.*, **A190**, 101 (1942).

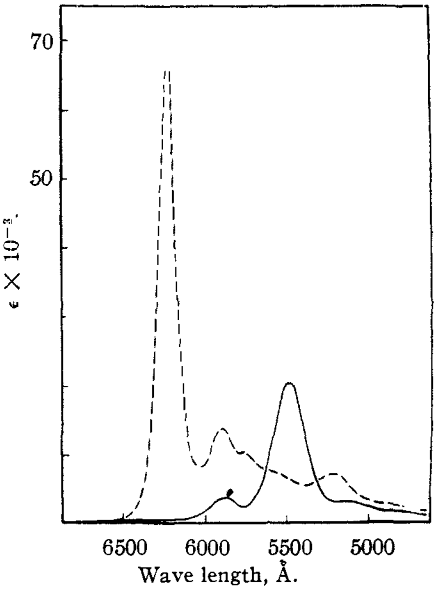

Fig. 3.—Zinc complex salts: solid line, component A, dotted line, component B (ε values for B should be multiplied by 0.833).

This ether solution of the B copper salt was evaporated to dryness in a test-tube and the crystals dissolved in about 10 cc. of glacial acetic acid. Excess copper acetate was added and molecular oxygen was bubbled through the solution for three to four minutes. The resulting copper complex was again transferred to ether, washed, dried, and the absorption maxima again measured at 6150 and at 5380 Å. This time the ratio of these values was 0.162 (see Fig. 2).

Reduction of the Zinc Salt of A.—A solution of the zinc salt of A was prepared by dissolving two or three milligrams of the A free base in 10 cc. of *n*-hexanol and heating the resulting solution with an excess of zinc acetate until a quantitative conversion to the zinc salt had been effected. The absorption spectrum of this solution is shown as curve A in Fig. 4. Reduction of this zinc complex was effected by boiling the alcohol solution and dropping into it small pieces of metallic sodium until the original deep violet-red color had changed to a faint green color characteristic of the B zinc complex. The spectrum of this reduced solution is shown as curve B in Fig. 4.

Reduction of the A Free Base.—One millimole of A free base was dissolved in 50 cc. of redistilled and hydrogenated dioxane, and the absorption spectrum measured on a diluted aliquot (shown as curve A in Fig. 5). This dioxane solution together with some palladium on barium sulfate as a catalyst was placed in the hydrogenation apparatus shown in Fig. 6. Chloroform was refluxed in the outer chamber of the apparatus to maintain the dioxane solution at constant temperature. The magnetic stirrer was started and the inner system pumped out and refilled with hydrogen. The hydrogenation was continued for seven hours after which time the dioxane solution was removed, filtered, and an aliquot taken on which the absorption spectrum was measured. This final spectrum is shown as curve B in Fig. 5.

The hydrogenation was followed quantitatively by measuring the decrease in pressure of the system *versus* time. The results led to nothing conclusive, however, due to the fact that the reduction is not clean cut, but continues beyond the first stage.

Analytical Results.[7]—Samples submitted for analysis were twice chromatographed and twice recrystallized from chloroform–methyl alcohol mixtures. Extreme care was taken to prevent the introduction of any extraneous carbonaceous material.

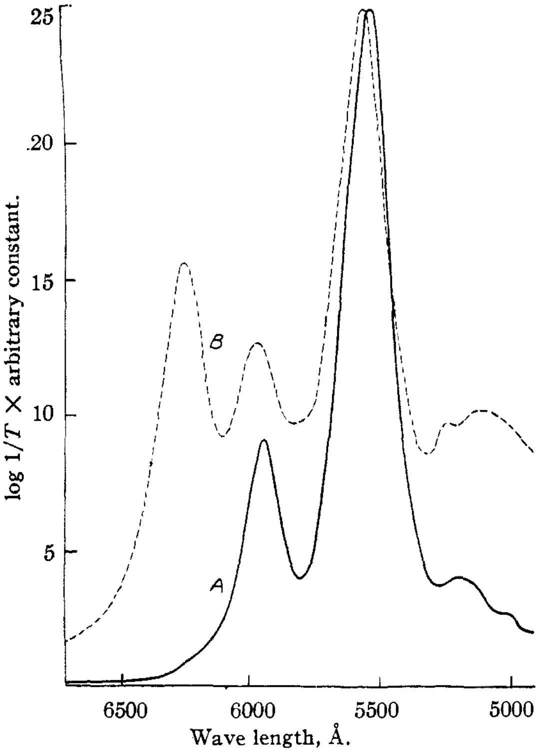

Fig. 4.—Reduction of Zn salt of A; solid line, Zn salt of A before reduction; dotted line, Zn salt after reduction with sodium.

Calcd. for tetraphenylporphine $C_{44}H_{30}N_4$: C, 85.96; H, 4.92. Found for material A

C	85.59	H	5.11
	85.32		4.94
	85.57		4.99
Av.	85.49	Av.	5.01

Calcd. for tetraphenylchlorin, $C_{44}H_{32}N_4$: C, 85.68; H 5.24. Found for material "B"

C	85.37	H	5.35
	85.40		5.31
Av.	85.39	Av.	5.33

Discussion

From the foregoing experiments, the oxidation–reduction relationship of compounds A and B has been established by three independent methods:

In the first experiment, the observed change in the ratio of the absorption coefficient at 6150 to that at 5380 Å. upon reference to the known absorption spectra for the copper salts of A and B, as shown in Fig. 2, leads to the conclusion that the B copper salt has been oxidized to the A copper salt.

In the second experiment, the absorption spectra of the solution of the zinc salt of A before and after reduction with sodium, Fig. 4, when compared with the known absorption spectra of the zinc salts of A and B as shown in Fig. 3 shows

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(7) The analyses were run by Mr. C. W. Koch.

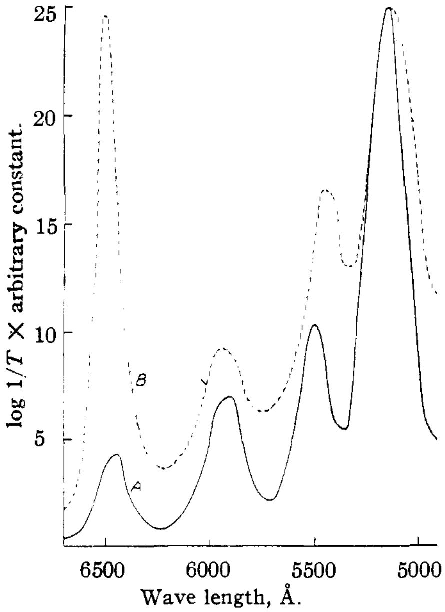

Fig. 5.—Reduction of free base A: solid line, A material before reduction; dotted line, same material after reduction with hydrogen.

that a substantial part of the A zinc salt has been reduced to the B zinc salt.

In the third experiment, the absorption spectra of the solution of the A free base before and after hydrogenation, Fig. 5, when compared with the known absorption spectra of the A and B free bases as shown in Fig. 1 shows that a substantial part of the A free base has been reduced to the B free base.

Finally, the analytical results confirm the oxidation-reduction relationship of materials A and B by showing the presence of additional hydrogen in material B.

Further investigation of these compounds is being continued in this Laboratory with special attention being paid to the correlation of structure and spectra, and to the applicability of this porphine-chlorin system in the study of photosynthesis.

Summary

1. It has been shown by three independent chemical methods and also by analysis that the two main products of the reaction of benzaldehyde and pyrrole are $\alpha,\beta,\gamma,\delta$-tetraphenyl porphine and $\alpha,\beta,\gamma,\delta$-tetraphenyl chlorin.

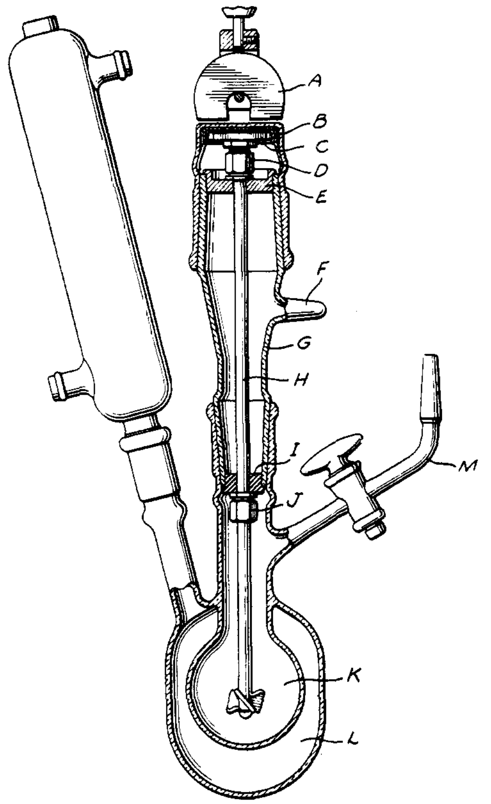

Fig. 6.—Hydrogenation apparatus: A, permalloy magnet; B, brass bearing surface; C, soft steel bar; D, brass clamp fitting; E, fiber bushing; F, hand grip to facilitate disassembly; G, center glass section (Pyrex); H, glass stirrer; I, fiber bushing; J, brass clamp fitting; K, reaction chamber; L, outer chamber; M, to gas buret and manometer system.

2. A direct synthesis of tetraphenyl porphine zinc complex is described. Through its use, practically pure tetraphenyl porphine can be prepared in yields of the order of twice that possible by direct synthesis.

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