

582. *Phthalocyanines and Related Compounds. Part XXI. The Oxidation of Phthalocyanine, Tetrabenzporphin, and Allied Substances.*

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It is shown that the oxidation of macrocyclic pigments of the phthalocyanine type in suspension in sulphuric acid proceeds in steps. A purple or brown intermediate is first formed. This subsequently undergoes hydrolysis, in the case of phthalocyanine, or further oxidation, in the case of pigments containing methin links. The initial reaction involves addition of oxygen, probably in the form of hydroxyl groups, and not dehydrogenation. The intermediate oxidation product from tetrabenzporphin is highly oxygenated and some fixation of sulphuric acid occurs.

The quantitative aspects of the complete oxidation of the pigments have been further studied. It is shown that the results diverge from a simple stoichiometric relationship in the case of the pigments containing many methin links.

It has been shown in previous papers that macrocyclic pigments of the phthalocyanine type are oxidised and hydrolysed in acid suspension by ceric sulphate (Dent, Linstead, and Lowe,

J., 1934, 1033; Barrett, Linstead, and Tuey, J., 1939, 1809; Barrett, Linstead, Rundall, and Tuey, J., 1940, 1079). The final products are phthalimide (or phthalic acid) together with ammonia from nitrogen links and carbon dioxide from methin links. The yield of the final products and the quantities of oxidising agent used afford evidence of structure and also a means of analysing mixtures of pigments.

All these oxidations actually proceed in steps and we have now made a preliminary examination of the intermediate stages. This is the main subject of the present paper, but before dealing with it we present below some additional data concerning the complete oxidations.

Tetrabenzporphins and tetrabenzazaporphins can all be represented by the general formula $C_{32}H_{18}N_4 + xN + (4 - x)CH$. The amount of oxygen theoretically required for oxidation to phthalimide and carbon dioxide is given by $1 + 4(4 - x)$ atoms. For example, tetrabenzmonoazaporphin ($x = 1$) requires 13 atoms of oxygen. In a previous paper (Barrett, Linstead, Rundall, and Tuey, *loc. cit.*) the following figures were given to summarise the quantitative oxidation of the various compounds.

Compound : $x =$	Phthalocyanine. 4	Tetrabenztriazaporphin. 3	Tetrabenzmonoazaporphin. 1	Tetrabenzporphin. 0
Atoms of oxygen used :				
Calc.	1	5	13	17
Found	1.0	4.8	12.5	16.2

These calculated figures assume a complete oxidation of the great ring and no oxidation of the benzene ring. We now find that in the comparatively long oxidations which are necessary for the compounds with many methin links, a perceptible oxidation of phthalimide occurs under the conditions of reaction. This is not true for phthalocyanine, which is oxidised within a few minutes at 60°: the oxidation of phthalimide in this case is negligible, and a result in agreement with the simple theory is obtained. But in the case of the methin-linked pigments a part of the observed uptake of oxygen is due to the oxidation of the aromatic rings and the figures given above need correction. This is small for the triaza-compound but may amount to up to 1 atom of oxygen for the less nitrogenous pigments. For example, new determinations on the oxidation of tetrabenzporphin—the purity of which was shown by analysis and by spectroscopic examination—showed that when the oxidation of phthalimide was corrected for by blank experiments, the oxygen uptake was only 14.5 instead of the calculated 17 atoms. This figure corresponds with complete disappearance of visible colour and with an apparent cessation of oxygen uptake. Possible explanations are either that a small amount of aerial oxidation occurs or (more probably) that colourless intermediate oxidation products are formed which involve the methin links. Perhaps some may persist as carboxylic acids.

The same effect can be seen to operate in the results tabulated below. These were obtained on pigments isolated from the reaction of phthalonitrile with successively larger amounts of methylmagnesium iodide.

Pigment.	1.	2.	3.	4.	
Moles of MgMeI per mole of nitrile	0.7	0.9	2.5	2.5	
Atoms of O required for oxidation (corr.)	5.3	5.5	9.0	10.4	
N, % found	{ 18.8 18.8 18.8	—	{ 15.5 15.4	14.4	
No. of CH links per molecule {	Calc. from oxidation	1.1	1.1	2.0	2.4
{ Calc. from N analysis	1.1	—	2.3	2.7	

Pigments 1 and 2 are clearly nearly pure tetrabenztriazaporphin. Pigments 3 and 4 contain considerable amounts of less nitrogenous macrocyclic pigment, so that statistically they correspond roughly to tetrabenzdiazaporphin. It will be observed that the number of methin links shown by oxidation of samples 3 and 4 is slightly smaller than that shown by nitrogen analysis. This indicates incomplete reaction.

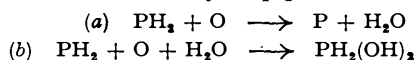
The results of oxidation of the compounds with more than one methin link do not therefore give completely precise information on structures, although they do enable a useful general estimate to be made.

Partial Oxidations.—Work in this field is made difficult by the unstable nature of the products, which cannot be crystallised or obtained with certainty in a state of purity. Some progress has, however, been made in the manner described below.

When a suspension of phthalocyanine in dilute sulphuric acid is treated in the cold with a small amount of oxidising agent (permanganate, ceric sulphate) the original blue colour changes immediately to a deep reddish-purple. On storage in the cold the purple solid passes into solution. Tetrabenztriazaporphin gives a similar purple solid, but its suspension is more stable and can be heated for several hours without complete decomposition. Tetrabenzmonoazaporphin and tetrabenzporphin resemble the triaza-compound, and are even more stable.

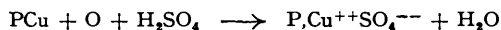
The amount of oxidising agent involved in the formation of the purple solid can be determined by treating the pigment at 0° with an excess of $N/20$ -ceric sulphate. After a suitable interval the solution is filtered and the excess of oxidizing agent is titrated with standard ferrous sulphate. In this way it can be shown that phthalocyanine takes up one atom of oxygen per molecule instantaneously, and the purple compound so formed does not react further at 0°. Tetrabenztriazaporphin and its copper derivative also take up one atom of oxygen immediately at 0°, but this is followed by a slow further uptake which presumably approaches the final value of 5 atoms theoretically required for complete oxidation. It is reasonable to suppose that the primary purple oxidation products from the two pigments, which are at a higher level of oxidation by one atom of oxygen per molecule, are formed by analogous reactions. The subsequent difference arises from the fact that the primary product undergoes hydrolysis in the case of phthalocyanine, and slow further oxidation in that of the triaza-compound.

The composition of the purple compounds was next examined. It seemed tolerably certain that no ring fission had occurred because the primary oxidation products regenerated the original pigments on treatment with ferrous sulphate or stannous chloride. Moreover, similar reductions occurred when attempts were made to crystallise the purple compounds from organic solvents. The oxygen must therefore act in one of two ways: either (a) it removes two hydrogen atoms (or the equivalent metal) from the centre of the great ring, or (b) it adds to the molecule, probably in the form of two hydroxyl groups. These two possibilities are represented below, where P denotes the molecule of macrocyclic pigment less the acidic hydrogen atoms:



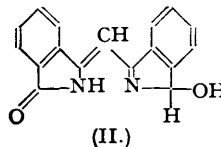
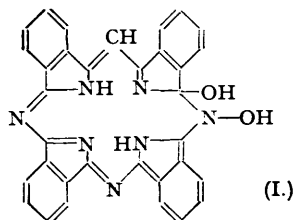
It has been shown experimentally that the hypothesis of dehydrogenation (a) cannot account for the oxidation of copper tetrabenztriazaporphin. Hence it is reasonable to suppose that it is also untrue for other compounds of this type. If the oxygen acted as a dehydrogenating agent then it would act on this copper pigment by forming a dehydro-compound with elimination of metal. Reduction of the intermediate would then yield a metal-free triaza-compound. Experiment shows that this is not true; reduction of the purple intermediate actually re-forms the original copper pigment.

However, this argument is not quite conclusive. The purple intermediate might be a complex copper sulphate, formed by dehydrogenation, in which the metal is co-ordinated with all four central nitrogen atoms:



If this explanation were true, reduction of the intermediate would regenerate the original copper compound, as experiment shows to be the case, but would at the same time liberate a molecule of sulphuric acid. Experiment showed that no sulphuric acid is formed.

It is therefore concluded that the initial action of oxygen must be one of addition (equation b), possibly the hydroxylation of a bridge double bond. Thus, the purple compound from tetrabenztriazaporphin might be (I). We endeavoured to confirm this by hydrolysing the purple intermediate from the triaza-compound into two molecules of



phthalimide and one molecule of diisoindolymethin (such as II). The purple compound was, however, stable to mild hydrolysing conditions. On more drastic treatment it disproportionated,

half yielding the original triaza-pigment and half dissolving. When two atoms of oxygen were used the purple pigment rapidly dissolved under hydrolysing conditions. Extraction of this acid solution with ether yielded rather more than the amount of phthalimide calculated for the above scheme. After basification, the solution yielded coloured tarry material which may possibly have corresponded to the oxidation products of the diisoindolylmethin. The corresponding simple isoindole bases are very susceptible to oxidation in ethereal solution (Linstead and Noble, *J.*, 1937, 933).

We next examined the much more complicated cases of tetrabenzporphin and tetrabenzmonoazaporphin. These substances give intermediate oxidation products which are brown rather than purple and are more stable towards reducing agents. The partial oxidation of tetrabenzporphin with acid ceric sulphate at 0° resulted in an uptake corresponding to about 9 atoms of oxygen per molecule in 12 hours. After this there was little further reaction. Similarly a sample of pigment, which from the nitrogen analysis contained 1.3 nitrogen links, took up 5 atoms of oxygen in about 6 hours at 0°, after which oxidation virtually ceased. These high figures for the oxygen uptake at 0° support the view that addition rather than dehydrogenation is involved.

It was not possible to purify these oxidation products by crystallisation or other conventional methods, and this made it impossible to ensure that homogeneous products were obtained or that the results of different preparations were exactly the same. However, the materials, dried to constant weight, gave analytical figures which, although varying to some extent from preparation to preparation, provided highly significant information. Thus the analytical figures for a sample of the oxidation product of tetrabenzporphin are shown below in comparison with those for the parent compound :

	C, %.	H, %.	N, %.	S, %.	O, % (by diff.).
Tetrabenzporphin	84.7	4.3	11.0	0	0
Oxidation product	59.0	4.05	7.7	4.04	25.2

It will be noted that the oxidation product contains sulphur, presumably present as a sulphuric ester of a hydroxyl group. If we assume that the oxidation product has suffered no loss of carbon or nitrogen from the molecule, then the molecular weight, calculated from the carbon or nitrogen values, is about 735. Even if all the sulphur is present as a sulphonic acid group, the great fall in carbon and nitrogen content cannot be accounted for from the introduction of such a group. An increase of 150 in the molecular weight is caused by addition of oxygen alone. This would correspond to about 9 atoms of oxygen (144) or 9 hydroxyl groups (153) and this agrees with the oxygen uptake, measured volumetrically.

In summary, the various evidence can all be accounted for on the following grounds : (1) the oxidation product of tetrabenzporphin is formed by the addition of 8 hydroxyl groups to four of the double bonds (probably the double bonds linking the rings) ; (2) this primary product undergoes slight further oxidation and there is some fixation of sulphuric acid, presumably by a hydroxyl group.

Unlike the parent compound, the oxidation product of tetrabenzporphin is completely soluble in dilute caustic alkali. The alkaline solution is green but shows no definite absorption spectrum. It regenerates the brown oxidation product on acidification. We could observe no reaction of the oxidation product with methyl sulphate, acetic anhydride, or hydrazine.

The oxidation product of tetrabenzporphin could be dissolved in pyridine and in acetone. The solutions showed the absorption spectrum of tetrabenzporphin. This must be formed by disproportionation. It cannot be present as an impurity because of the complete solubility of the oxidation product in alkali. Spectroscopic assay shows that about one-third of the oxidised pigment is converted back into tetrabenzporphin in pyridine solution. This is consistent with the analytical figures : 3 moles of the primary oxidation product of tetrabenzporphin will contain about $3 \times 9 = 27$ atoms of oxygen, which is approximately the amount required for complete oxidation of two moles of the pigment ($2 \times 14.5 = 29$ atoms).

Because of their lability, it is difficult to advance structures for compounds of this type with any certainty. The proposals which are made above, although satisfactory, are not unique, and the formation of carbonyl groups on the *meso*-carbon atoms is not excluded.

These results may be compared with those from the oxidation of porphyrins observed by Hans Fischer. He obtained, for example, a yellow tetroxide and a colourless dioxide from *ætioporphyrin*, but these failed to react with carbonyl or hydroxyl reagents [Fischer and Stern, "Die Chemie des Pyrrols," Vol. II, (2), p. 423].

Attempted Simulation of Lemberg's Oxidations.—Lemberg (*Biochem. J.*, 1935, 29, 1322) has

shown that hæmin undergoes fission of the great ring when treated with oxygen in an aqueous pyridine solution containing hydrazine. After a series of changes the bile pigment biliverdin, which contains a chain of four pyrrole units, is ultimately obtained. We attempted the same type of oxidation by passing oxygen through a pyridine solution of ferrous tetrabenzporphin, using hydrazine as substrate, but no reaction was observed even at 80°. With glucose as substrate, the green solution slowly became brown and a weak band developed with maximum at 6220 Å. No definite product could, however, be isolated; neither could definite results be obtained by the use of either benzaldehyde or maleic anhydride as substrate. A solution of ferrous phthalocyanine in pyridine containing hydrazine changed from green to brown when oxygen was passed through it, but no definite spectrum appeared.

EXPERIMENTAL.

(1) *Materials*.—Metal-free tetrabenztriazaporphin was prepared following Barrett, Linstead, and Tuey (*loc. cit.*) and crystallised from chloronaphthalene. Tetrabenzmonoazaporphin was made from phthalonitrile and methylmagnesium iodide (2½ moles) (Barrett, Linstead, Rundall, and Tuey, *loc. cit.*). It was crystallised from chloronaphthalene and sublimed at 3 mm. Zinc tetrabenzporphin was prepared as described in the preceding paper. The copper tetrabenztriazaporphin was a sample prepared by Dr. G. A. P. Tuey. The phthalocyanine was an analytically pure reference sample.

(2) *Complete Oxidations*.—Quantitative oxidations were carried out in Erlenmeyer flasks covered by watch-glasses and heated in a boiling-water bath. Approx. 50 mg. of the pigment were weighed out accurately, dissolved in 5 c.c. of concentrated sulphuric acid, and precipitated by the addition of 30 g. of ice made from distilled water. 50 c.c. of N/20-ceric sulphate were added, the solution was heated for the required time, cooled, treated with 50 c.c. of N/20-ferrous sulphate, and back titrated with N/20-ceric sulphate. Phenanthroline-ferrous sulphate was used as indicator and was preferable to diphenylamine. The colour change is from red to green and is sensitive to 0.02 c.c. of N/20-ceric sulphate.

The following blank experiments were carried out. Ceric sulphate was unchanged under the reaction conditions when heated at 100° for 2 hours either alone or with ammonium sulphate. Experiments with phthalimide equivalent to 50 mg. of pigment were carried out, a concentration of ceric sulphate being used which corresponded to that prevailing at the end of a quantitative oxidation of pigment. The blank reaction after various periods at 100° is shown below, the results being expressed in atoms of oxygen per 4 moles of phthalimide:

Time (hours)	1	1.5	2	4	6	8
Uptake of oxygen	0.2	0.3	0.4	0.8	1.4	1.7

Willard and Young (*J. Amer. Chem. Soc.*, 1930, **52**, 132) found that ceric sulphate slowly attacks phthalic acid at 95°.

Tetrabenztriazaporphin (metal-free) gave the following oxidation figures under the above conditions. The third line gives the uptake of oxygen corrected for the oxidation of phthalimide.

Time (mins.)	60	80	100	120	140
Uptake of oxygen (atoms), obs.	5.4	5.5	5.5	5.7, 5.8	5.8
" " " corr.	5.2	5.2	5.2	5.3, 5.4	5.3

The number of methin links calculated from the value of 5.3 atoms of oxygen is 1.1. This sample of triaza-pigment had been prepared from methylmagnesium iodide and an excess of phthalonitrile (1.4 moles). The nitrogen content was 18.8%, whereas that calculated for pure tetrabenztriazaporphin is 19.1%. On the assumption that the material is the triaza-compound containing a small amount of less nitrogenous pigment of the $C_{32}H_{18}N_4 + xN + (4 - x)CH$ series, it is possible to calculate the number of methin links from the nitrogen analysis. This gives a figure of 1.1 in agreement with the result of oxidation.

Tetrabenzmonoazaporphin (metal-free) gave the following oxidation figures under the same conditions:

Time of reaction (mins.)	90	110	130	150
Uptake of oxygen (atoms), obs.	10.2	10.8	10.9	10.7
" " " corr.	9.9	10.4	10.5	10.2

The figure of 10.4 atoms of oxygen corresponds to 2.4 methin links. This sample of tetrabenzmonoazaporphin had N, 14.4% (Calc. for $C_{35}H_{21}N_5$: N, 13.7%). This nitrogen figure corresponds to 2.7 methin links.

Another sample of "monoaza"-pigment showed an oxidation figure (corrected) of 9.0 atoms in 150 minutes, corresponding to 2.0 methin links. The nitrogen content was 15.5%, corresponding to 2.3 methin links.

Zinc tetrabenzporphin gave the following oxidation figures. The theoretical oxygen uptake is 17.0 atoms, assuming no oxidation of the benzene rings and complete oxidation of the great ring.

Time of reaction (mins.)	155	215	540	570
Uptake of oxygen (atoms), obs.	14.6	15.4	15.5	16.0
" " " corr.	14.1	14.6	13.6	14.1

The products of this oxidation were isolated as follows: 500 mg. of zinc tetrabenzporphin were treated with 800 c.c. of *N*/20-ceric sulphate at 100° for 10 hours. An excess of ferrous sulphate was added and the solution was continuously extracted with ether. Evaporation of the ether left 360 mg. (65%) of phthalic acid, m. p. 190—195°, identified as the anhydride, m. p. and mixed m. p. 129—130°. When the solution was made basic, cerium and iron were precipitated as hydroxides. The precipitate was filtered off, dried, and extracted with ether (Soxhlet), and the basic filtrate was also continuously extracted with ether. The combined extracts on evaporation yielded a few mg. of a light red oil. On treatment with methanol and hydrochloric acid this was converted into a microcrystalline colourless solid, but the amount was too small for further investigation.

(3) *Partial Oxidations*.—50 mg. of phthalocyanine were dissolved in 10 c.c. of sulphuric acid and quenched with 50 g. of ice, prepared from distilled water. The fine blue suspension was stirred at 0°, and 50 c.c. of *N*/20-ceric sulphate were introduced. At the end of the reaction the purple suspension was removed on sintered glass, and the filtrate treated with 50 c.c. of *N*/20-ferrous sulphate and back-titrated with *N*/20-ceric sulphate (phenanthroline). The uptake of oxygen during reaction periods of 1—10 minutes corresponded to 1.0 atom. This figure is the same as that found by Dent, Linstead, and Lowe (*loc. cit.*) for the complete oxidation.

Tetrabenztriazaporphin (metal-free; complete oxidation figure at 100°: 5.4 atoms of oxygen) was similarly treated. The uptake of oxygen increased with time as follows:

Time (hours)	1	1.5	2.5	6
Oxygen uptake (atoms)	1.2	1.3	1.5	1.55

A second sample of the same pigment with a complete oxidation figure at 100° of 5.8 atoms of oxygen gave the following figures for partial oxidation at 0°:

Time (hours)	0.5	1	2	6	12
Oxygen uptake (atoms)	1.5	1.6	1.6	1.85	2.2

These figures, which give an approximately linear plot, were obtained by the use of a considerable excess of ceric sulphate (about 15 moles), and the concentration of this therefore remained effectively constant. When the second sample of tetrabenztriazaporphin was oxidised with only 10 c.c. of the ceric sulphate (about 3 moles) a curve was obtained:

Time (hours)	0.5	0.75	1.0	1.5	2.0	3.0	5.0
Oxygen uptake (atoms)	0.6	0.8	1.0	1.25	1.45	1.5	1.65

Partial-oxidation Products of Tetrabenztriazaporphin.—(1) The following experiment was designed to see if it were possible to hydrolyse the purple substance obtained by the addition of one atom of oxygen to tetrabenztriazaporphin. 35 mg. of the pigment in acid suspension at 0° (10 c.c. of sulphuric acid, 12 g. of ice) were treated with an amount of *N*/20-ceric sulphate exactly equivalent to one atom of oxygen. After 10 minutes the mixture was heated, and the purple suspension changed rapidly to green. This apparently corresponds to a disproportionation which regenerates some tetrabenztriazaporphin and yields a product at an oxidation level of 2 atoms of oxygen which goes into solution. The same result was obtained when 6*N*-sulphuric acid was used.

(2) Tetrabenztriazaporphin dissolves readily when its suspension in sulphuric acid is treated with 2 atoms of oxygen. 800 mg. of the pigment in acid suspension (50 c.c. of sulphuric acid, 150 g. of ice) were treated with 130 c.c. (2 atoms) of *N*/20-ceric sulphate solution. The mixture was left at 0° for 10 minutes and then heated on the steam-bath for the same time. The yellow solution was then filtered from a small brown residue (about 20 mg.), treated with ferrous sulphate, and extracted continuously with ether for 16 hours. The extract yielded 550 mg. of phthalimide (m. p. and mixed m. p.). The weight of phthalimide which is theoretically obtainable from the fission of 3 nitrogen links would be 475 mg. The residual aqueous solution was made alkaline, the precipitate of inorganic hydroxides was filtered off and extracted with ether (Soxhlet), and the basic filtrate extracted continuously with ether. The green extracts were combined and evaporated; they yielded a brown tar giving a brown solution in methanolic hydrochloric acid. No crystalline products could be isolated.

Partial-oxidation Product from Copper Tetrabenztriazaporphin.—The copper tetrabenztriazaporphin used had N, 16.7% (corresponding to 1.16 methin links) and a complete oxidation figure at 100° of 4.4 atoms (corresponding to 0.8 methin link). The partial oxidation figure in 1 hour at 0°, determined as described above, was 1.0 atom.

480 mg. of this compound were dissolved in sulphuric acid (20 c.c.) and quenched with ice (50 g.). The suspension was treated with 100 c.c. of *N*/20-ceric sulphate solution, and the mixture left at 0° for 1 hour with occasional shaking. The purple solid was then collected on sintered glass and washed with very dilute hydrochloric acid until the washings were free from sulphate. Washing with pure water led to the formation of a very fine suspension which passed through the filter.

The purple solid was reduced by stannous chloride solution (2 g. of dihydrate in 200 c.c. of *N*/10-hydrochloric acid) which regenerated copper tetrabenztriazaporphin (230 mg.) indistinguishable from the starting material. The filtrate gave a precipitate of barium sulphate which weighed 2 mg., whereas the amount which would have resulted from the decomposition of an equivalent amount of a pigment $P_2Cu^{++}SO_4^{--}$ is 94 mg.

Partial Oxidations of Tetrabenzmonoazaporphin and Tetrabenzporphin.—These were carried out as described for tetrabenztriazaporphin except that the weight of pigment was only 10 mg. The monoazapigment contained 2.7 methin links from the nitrogen analysis. It gave the following figures at 0°:

Time (hours)	5	7.5	10	20
Oxygen uptake (atoms)	5.0	5.0	5.0	5.6

Sublimed tetrabenzporphin gave the following partial oxidation figures :

Time (hours)	3	5	8	14	15	25
Oxygen uptake (atoms)	7.7	8.7	9.5	9.6	9.6	10.0

Oxidation Product of Tetrabenzporphin.—400 mg. of tetrabenzporphin were dissolved in 30 c.c. of sulphuric acid, precipitated with 100 g. of ice, and partially oxidised for 4 hours at 0° with 350 c.c. of N/20-ceric sulphate solution. The brown suspension was filtered off on hardened paper and washed at 0° until free from sulphate. The filtrate gave a red colour with phenanthroline which indicated that all the ceric sulphate had been consumed (oxygen uptake 10.7 atoms). The oxidised pigment was dried over phosphoric oxide at 25°/0.5 mm. for several days to constant weight; the yield was 114 mg. of a brown amorphous solid (Found : C, 59.0; H, 4.05; N, 7.8, 7.65; S, 4.0%). On treatment of this material with dilute aqueous potassium hydroxide, it went into solution immediately to give a green solution with no characteristic absorption bands. Acidification of the solution re-formed the brown solid. Cold pyridine dissolved oxidised tetrabenzporphin at once to a deep green solution with the spectrum of tetrabenzporphin. From the intensity of the band at 6200 Å., the weight of tetrabenzporphin formed was equal to 35% of that of the oxidised pigment.

Two other samples of oxidised tetrabenzporphin were prepared, shorter times of reaction being used. These less oxygenated materials behaved differently towards aqueous alkali as indicated below :

Oxygen uptake (atoms)	10.7	7.8	5.3
Solubility in KOH	Soluble	Soluble	Partly soluble
Colour of alkaline solution	Green	Brown	Yellow

The colour of the alkaline solution of the intermediate sample (7.8 atoms oxygen) was converted at once into the green of the more highly oxidised state by addition of a few drops of alkaline permanganate solution.

Attempted Oxidations of Ferrous Pigment by Atmospheric Oxygen.—Ferrous tetrabenzporphin, prepared by Barrett, Linstead, Rundall, and Tvey's method (*loc. cit.*), had absorption maxima at 596, 574, and 550 mμ., as previously reported. 50 mg. were dissolved in 10 c.c. of pyridine and 0.5 c.c. of water and treated with 6 drops of hydrazine hydrate (85%). A rapid stream of oxygen was passed through the solution at 80°. No change could be observed in the spectrum or in the visual colour of the solution.

A solution of 300 mg. of ferrous tetrabenzporphin in 50 c.c. of pyridine was heated to 80°, and a vigorous stream of oxygen was passed through it. A dilute aqueous solution of glucose was introduced dropwise during 7 days. At the end of this time the colour of the pyridine solution had changed from green to red-brown. The ferrous tetrabenzporphin bands had disappeared from the spectrum, which now showed a weak maximum at 6260 Å. and diffuse absorption in the far violet. Attempts to separate a definite product by chromatography or crystallisation were fruitless. Similar changes were observed when ferrous phthalocyanine was treated in the same way.

The nitrogen analyses described in this paper were carried out by the Kjeldahl method, no catalyst being necessary. The ammonia was distilled into 4% boric acid solution, following Meeker and Wagner (*Ind. Eng. Chem., Anal.*, 1933, **5**, 396; 1934, **6**, 473).

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