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Reversible Oxidation of Phthalocyanines

C. J. PEDERSEN*

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Phthalocyanines can be reversibly oxidized in nonaqueous media to substances soluble in organic solvents and from which the phthalocyanines can be regenerated by reduction. Several different classes of suitable oxidizing agents were found. The properties of the oxidation products suggest that they are formed by the addition of a molecule of the oxidant to the phthalocyanine molecule but modified by solvolysis in the case of reactive solvents. Zinc $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine can also be reversibly oxidized in benzene by benzoyl peroxide.

The oxidation of phthalocyanines has been reported by several investigators.¹⁻⁸ In these studies the oxidation was mostly destructive because either the oxidants or the conditions were not suitable for the formation of reversible oxidation products except in traces or only as transient intermediates which were rapidly hydrolyzed. In no case was the oxidation product isolated and analyzed.

More recently, however, F. Baumann and his colleagues have described^{9,10} products obtained by reacting a mole of copper phthalocyanine or cobalt phthalocyanine with a great excess of one of two oxidizing agents: eleven moles of bromine in methanol or fifteen moles of concentrated nitric acid in nitrobenzene. The final products are soluble in organic solvents, are reduced to phthalocyanines, and are related to the oxidation products discussed in this paper.

The operable oxidants which were tested can be divided into four groups: peroxides and hydroperoxides¹¹; chlorine and bromine^{12,13}; organic hypochlorites¹⁴; and N-halogen compounds. The methods of preparing reversible oxidation products of

phthalocyanines with these oxidants have already been described in the indicated references, but additional work, particularly with benzoyl peroxide, has shed new light on the subject.

It was found that benzoyl peroxide reacts with copper phthalocyanine in chloroform, very much faster than its rate of spontaneous decomposition, to give well defined oxidation products.

More specifically, about 70% of the benzoyl peroxide (initial concentration: 0.14 molar) reacts with an excess of finely divided copper phthalocyanine in U.S.P. chloroform (0.57% by weight of alcohol) at 30° within the first 2 hr. This rate is about 1800 times greater than the rate of spontaneous decomposition of the peroxide in chloroform at the same temperature as determined by Cass.¹⁵ No carbon dioxide is evolved and the rate is not affected by the presence or absence of molecular oxygen. The rate, however, is about 60% lower in pure chloroform and the oxidation product, instead of yielding a bright pigment on reduction as in the case of the product obtained in chloroform containing alcohol, gives a dull, dark blue precipitate.

Although no accurate rate measurement was made, it was evident that the relative order of reactivity of the peroxides is: bis(2,4-dichlorobenzoyl) peroxide > bis(4-chlorobenzoyl) peroxide > benzoyl peroxide.

It is concluded from these facts that the reaction between benzoyl peroxide and copper phthalocyanine (I, Fig. 1) does not involve the initial decomposition of the peroxide into benzoate free radicals, but that the decomposition of the peroxide is induced by the phthalocyanine as in the reactions discussed by several investigators.¹⁷⁻²⁰ The high rate of reaction, the absence of carbon dioxide, and the relative order of reactivity of the peroxides are consistent with this type of reaction.

The course of the reaction is shown in Fig. 4. The

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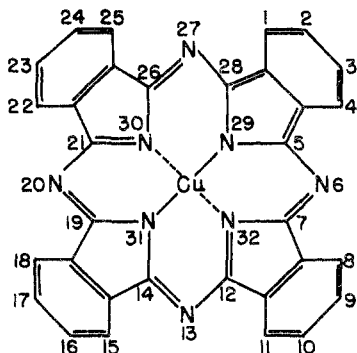
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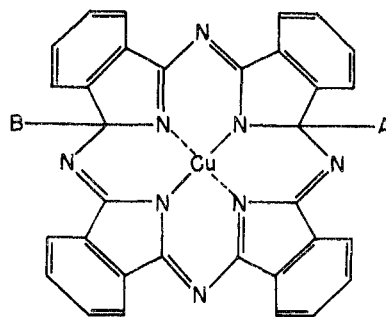
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upper right hand portion of Fig. 1 represents the phthalocyanine molecule, A:B the oxidant, the broken arrows indicate the movement of a single electron, and the solid curved arrow the movement of a pair of electrons. In certain respects this mechanism is similar to the one proposed by Horner and Betzel¹⁹ for the reaction between benzoyl peroxide and trialkylamines.

Fig. 1.—I¹⁰

It will be noted that the *o*-quinoid ring is changed into an *o*-phenylene ring and a carbonium ion is formed with the electron-deficient carbon atom at position 28. The reaction occurs more readily in the presence of alcohol because an ion is formed. By the movement of other pairs of electrons, the electron-deficient carbon atom can also be located at equivalent positions 26, 21 or 19 without converting any of the *o*-phenylene rings into an *o*-quinoid ring. Position 21 is thought to be the most favorable because the molecule can then be folded along the 5-21 axis thus destroying the extensive resonance of the planar phthalocyanine molecule without distorting too much the central coordination system consisting of the metal and the four nitrogen atoms. Observe that no ring is broken in this reaction.

The carbonium ion resulting from the reaction of benzoyl peroxide and copper phthalocyanine can react in several ways. In the absence of enough hydroxylic solvent it reacts with the benzoate anion forming II, A and B = benzoate Fig. 2. Since atoms 5 and 21 are allylic, the benzoate groups can be replaced by alkoxy groups. Hence, by diluting the chloroform solution of the oxidation product with methanol, II, A = benzoate, B = methoxy is first formed and then II, A and B = methoxy. The products which are actually recovered are in agreement with these structures.

Fig. 2.—II²¹

A dark, reddish brown solution is obtained by filtering the reaction mixture of copper phthalocyanine and benzoyl peroxide in U.S.P. chloroform at the end of 2 hr. If this solution is concentrated and diluted with methanol, a product is rapidly deposited whose composition corresponds to that of II, A = benzoate, B = methoxy, and another

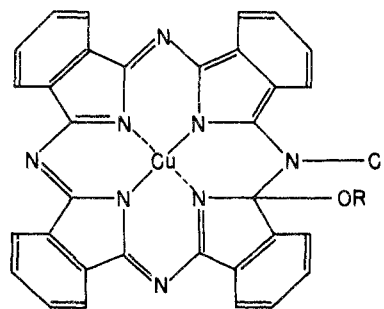


Fig. 3.—III

crop of crystals is recovered from the filtrate on long standing whose composition corresponds to that of II, A and B = methoxy. These products are less soluble in methanol than in chloroform, are hydrolyzed by mineral acid to give four moles of phthalimide and four moles of ammonia per mole, and yield the expected amount of copper phthalocyanine on reduction.

These structures are also supported by the infrared spectra. Fig. 5a is the infrared spectrum of II, A = benzoate, B = methoxy and Fig. 5b is that of II, A and B = methoxy. The basic pattern of the two spectra is the same and the region covered by 6.0-6.3 μ is consistent with the presence of two different types of C=N bonds (the peripheral and the inner, respectively), and the aromatic C=C bond. The strong band at 5.8 μ in Fig. 5a is evidence for the presence of the benzoate group and the

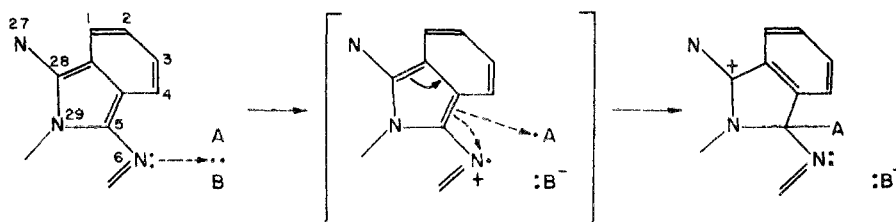


Fig. 4.—IV

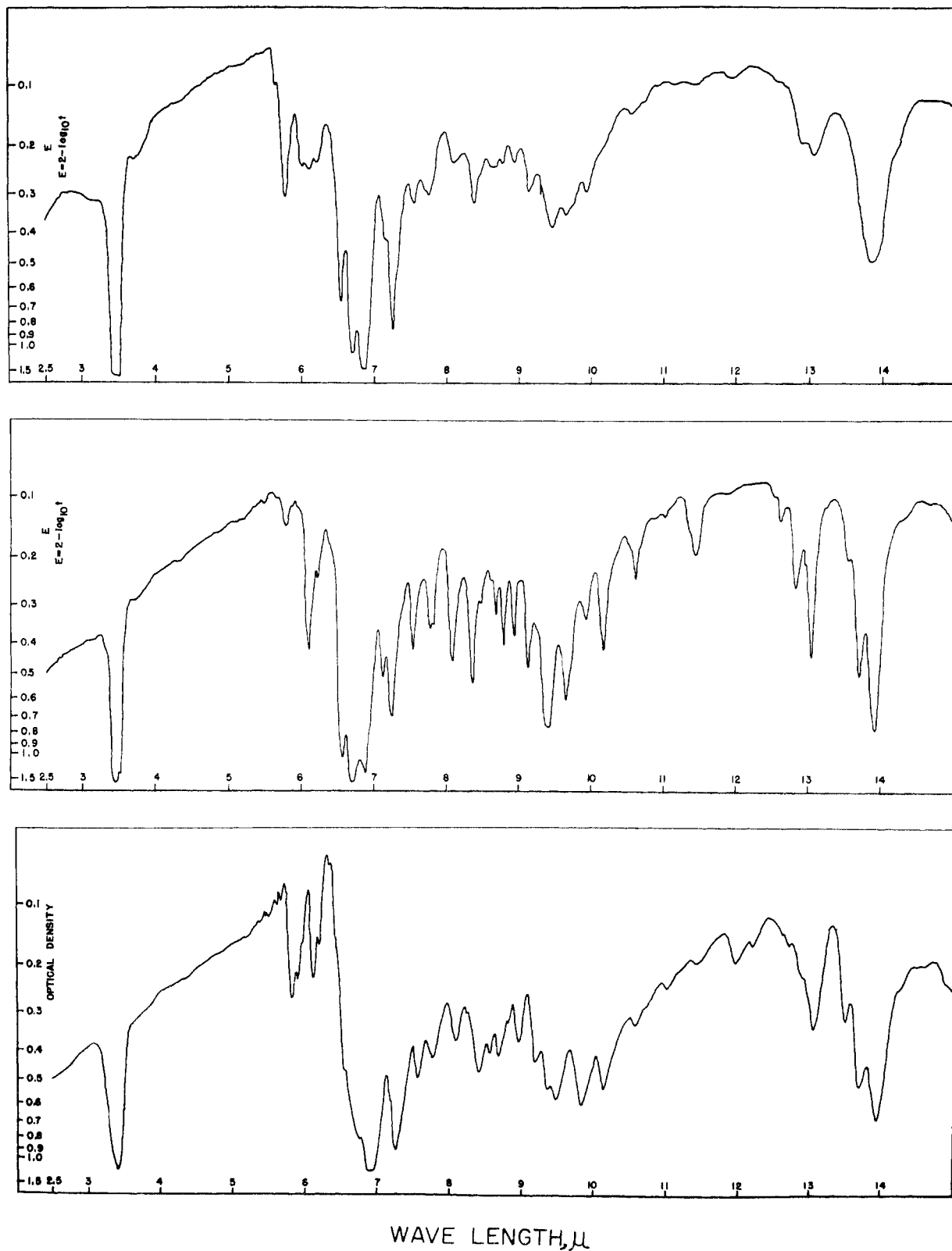


FIG. 5.—INFRARED SPECTRA OF THE REVERSIBLE OXIDATION PRODUCTS OF COPPER PHTHALOCYANINE. Nujol mull, 0.025 mm., NaCl prism. Top: (Fig. 5a), (Fig. 2, A = benzoate, B = methoxy). Middle: (Fig. 5b), (Fig. 2, A and B = methoxy). Bottom: (Fig. 5c), (Fig. 3, R = *t*-butyl).

weak band at 8.9μ suggests the presence of C—O—CH₃. The 5.8μ band in Fig. 5b is much weaker indicating the possibility that the carbonyl band is

due to a minor constituent, and the stronger band at 8.9μ is consistent with the presence of two C—O—CH₃ groups.

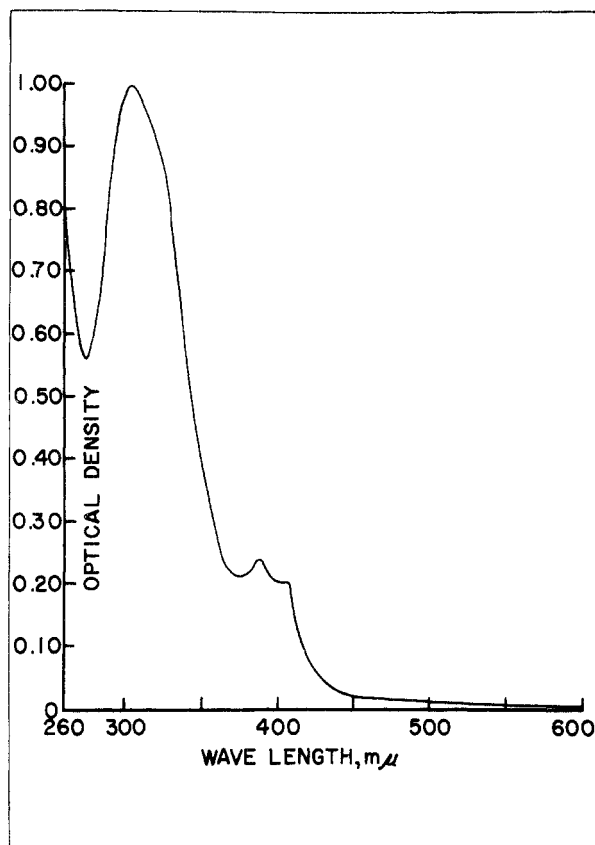


FIG. 6.—ULTRAVIOLET SPECTRUM OF (FIG. 2, A AND B = METHOXY). One centimeter chloroform solution. 0.0156 gram per liter (2.45×10^{-5} molar). Extinction coefficient = 41,000 at 304 $m\mu$.

In contrast to phthalocyanines which are blue or green solids of high tinctorial power, the reversible oxidation products are yellowish or reddish solids of low tinctorial power. Fig. 6 is the ultraviolet spectrum of II, A and B = methoxy. It has a peak at 304 $m\mu$ and is nearly identical with the spectrum of II, A = benzoate, B = methoxy.

The reaction of phthalocyanines with chlorine in methanol follows a similar course. Mixtures of II, A = chlorine, B = methoxy and II, A = hydroxyl, B = methoxy are obtained by reacting copper phthalocyanine with chlorine^{12,18} and drowning the filtrate in aqueous sodium carbonate or sodium hydroxide. In this case the initial carbonium ion reacts with methanol to give II, A = chlorine, B = methoxy some of which is converted into II, A = hydroxyl, B = methoxy by the base. The ultraviolet spectra of these products are also very similar to Fig. 6.

The elementary analyses of the crystalline oxidation product, obtained by reacting copper phthalocyanine and *tertiary*-butyl hypochlorite¹⁴ in methanol, correspond to those of III, R = *t*-butyl. Fig. 7 is its ultraviolet spectrum and Fig. 5c is its infrared spectrum.

Note that the structure of this oxidation product is different from that of the others: the chlorine is

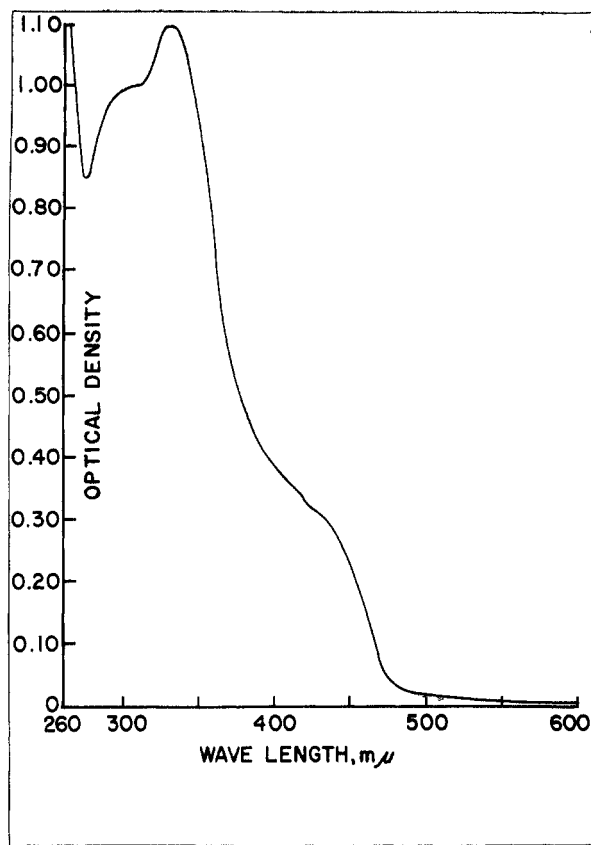


FIG. 7.—ULTRAVIOLET SPECTRUM OF (FIG. 3, R = TERTIARY-BUTYL). One centimeter chloroform solution. 0.0241 gram per liter (3.52×10^{-5} molar). Extinction coefficient 28,000 at 302 $m\mu$ and 31,000 at 330 $m\mu$.

on a peripheral nitrogen atom and there is an *o*-quinoid ring in the molecule. Fig. 3 shows the occupation of positions 6 and 7 by the substituents, but isomers are possible at positions 6-12, 6-14, and 13-14. The chlorine is thought to be on the nitrogen atom because chlorine gas is generated when it is treated with concentrated sulfuric acid, and although it contains no chlorine which reacts with caustic or silver nitrate, chloride ions are found in the filtrate after its reduction to copper phthalocyanine with a reducing agent free from chloride ions. Its ultraviolet spectrum has peaks at 302 $m\mu$ and 330 $m\mu$, the latter not being found in the spectra of the others. Its infrared spectrum resembles Fig. 5b more closely than Fig. 5a. The strong absorption in the region of 5.8-6.0 μ cannot be accounted for since it is almost certain that none of the carbon atoms of the phthalocyanine molecule has been changed into a carbonyl group, an event which requires the opening of one of the non-benzonoid rings.

It is concluded, therefore, that hypochlorites merely add to a peripheral C=N bond or one of its conjugated equivalents, the chlorine going on the nitrogen atom. The N-halogen oxidants might also react in this manner but, aside from establishing the formation of reversible oxidation products, no

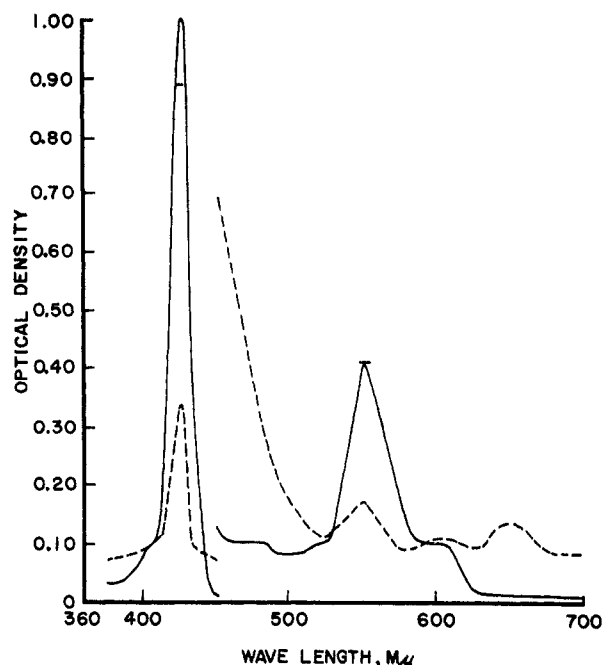


FIG. 8.—ULTRAVIOLET SPECTRUM OF ZINC $\alpha,\beta,\gamma,\delta$ -TETRAPHENYLPORPHINE. One centimeter thiophene-free benzene solutions. Concentration up to 450 $m\mu$: 0.00197 gram per liter (2.9×10^{-6} molar). Concentration above 450 $m\mu$: 0.0197 gram per liter (2.9×10^{-5} molar). Solid line—before reaction with benzoyl peroxide; Extinction coefficient 345,000 at 425 $m\mu$ and 14,100 at 550 $m\mu$. Dashed line—after reaction with 8.2×10^{-6} molar benzoyl peroxide at 24–27° for 20 hr. in the dark. Short horizontal lines at 425 $m\mu$ and 550 $m\mu$ indicate the extent of recovery of the absorption bands at these wave lengths on treating the oxidized solution with ascorbic acid.

further work was done with this class of oxidants.

The reversible oxidation of zinc $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine²² was briefly investigated spectrophotometrically without isolating the oxidation product. The compound is oxidized in benzene by benzoyl peroxide to an unidentified product from which the original compound is regenerated by methanolic ascorbic acid. The porphine, however, is irreversibly oxidized if allowed to remain in contact with an excess of benzoyl peroxide. The ultraviolet spectra of zinc $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine and its oxidation product are shown in Fig. 8.^{23–27}

EXPERIMENTAL

Tertiary-butyl hypochlorite was prepared according to

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Teeter and Bell.²⁸ Pure chloroform was made from U.S.P. chloroform by the conventional method. All other materials were either laboratory samples or commercial products used without further purification. No accurate rate measurements were made because it was difficult to establish and maintain standard conditions, especially to control the particle size of the phthalocyanines.

The ultraviolet and visible spectra were determined with a Cary Model 11 Recording Spectrophotometer. The infrared spectra were obtained with a Perkin-Elmer Model 12-C Spectrophotometer. The identities of the phthalocyanines recovered by reduction were determined by x-ray diffraction²⁹ with a Norelco 90° Diffractometer using Cu K α radiation.

Copper phthalocyanine and benzoyl peroxide. Twenty-one and three-tenths g. of α -copper phthalocyanine (0.037 mole), range of particle size 0.05 to 0.1 μ , found: N, 19.7; Cu, 10.8; required: N, 19.5; Cu, 11.0) and 7.02 g. of benzoyl peroxide (0.029 mole) in 217 ml. of U.S.P. chloroform containing 1.84 g. of ethanol (0.04 mole) were agitated on a magnetic stirrer for 2 hr. at 27–30°. The flask was connected to a gas bubbler containing aqueous barium hydroxide and showed that no gas was evolved during the reaction. The temperature was maintained spontaneously.

The reaction mixture was filtered and the unreacted phthalocyanine was washed with chloroform and dried. It weighed 9.95 g. Hence, 11.35 g. of phthalocyanine (0.0197 mole) had dissolved. Since there was no direct method of determining the peroxide in the reaction mixture, it was assumed that it took a mole of peroxide to dissolve a mole of phthalocyanine. On this basis 0.0197 mole of peroxide had reacted in 2 hr. or 68%.

The following data were obtained by aliquoting the filtrate but they are presented as if the entire sample had been used for each analysis.

The filtrate (296 ml.) contained 10.5 g. of copper phthalocyanine (0.0182 mole) recoverable by reduction with ascorbic acid. The filtrate was evaporated under vacuum to about 30 ml. and stirred into 300 ml. of anhydrous methanol. The precipitate which formed rapidly was filtered and dried at 85°. Four and nine-hundredths g. of greenish brown powder (0.0056 mole) were obtained.

Anal. Calcd. for II, A = benzoate, B = methoxy (Fig. 2), C₄₀H₂₄CuN₈O₃: N, 15.4; Cu, 8.73; phthalimide, 80.5; ammonia, 9.3; copper phthalocyanine, 79.1; benzoic acid, 16.75. Found: N, 15.8; Cu, 9.1; phthalimide, 73; ammonia, 8.8; copper phthalocyanine, 68; benzoic acid, 10.8.

Another crop of crystals was obtained from the last filtrate on standing overnight at room temperature. Three and eighty one-hundredths g. of purplish brown crystals (0.006 mole) were recovered by filtering and drying at 85°.

Anal. Calcd. for II, A and B = methoxy, C₃₄H₂₂CuN₈O₂: N, 17.58; Cu, 9.96; phthalimide, 91.8; ammonia, 10.65; copper phthalocyanine, 90.4. Found: N, 17.2; Cu, 9.8; phthalimide, 82; ammonia, 11.64; copper phthalocyanine, 87.

Phthalimide was determined gravimetrically by hydrolyzing 0.5 g. of the oxidation product with 20 ml. of methanol and 2 ml. of concentrated hydrochloric acid for 10 min. at room temperature, then adding 80 ml. of water and concentrating on a steam bath to 45 ml. The suspension was chilled in ice water, the crystals of phthalimide were collected on a Gooch crucible, dried, and weighed. They melted at 235° (lit. 238°) and contained 9.4% N; required for C₈H₅N₂O₂: N, 9.5.

Ammonia was determined by making the filtrate from the phthalimide analysis alkaline with sodium hydroxide

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and distilling off the ammonia into standardized hydrochloric acid.

Copper phthalocyanine was determined gravimetrically by dissolving 0.5 g. of the oxidation product in 50 ml. of methanol, adding 0.25 g. of ascorbic acid and warming on a steam bath for 20 min. One hundred fifty ml. of water were then added, neutralized with sodium carbonate, heated for 1 hr., filtered, washed with methanol and ether, and dried at 85°. The blue crystals were identified as *alpha*-copper phthalocyanine by x-ray diffraction. It took 1.2 moles of ascorbic acid to reduce a mole of the oxidation product, and the excess is thought to be due to the difficulty of the end point.

Benzoic acid was estimated by concentrating the filtrate from the copper phthalocyanine analysis to 100 ml., acidifying with sulfuric acid, extracting with ether, and evaporating to dryness. The white crystals obtained by recrystallizing the residue melted at 122°; mixed melting point with an authentic sample of benzoic acid 122°.

Similar results were obtained when the reaction was run in an atmosphere of nitrogen instead of air. When purified chloroform was substituted for the U.S.P. material, 0.0082 mole of benzoyl peroxide reacted in 2 hr. and the filtrate contained only 1.36 g. of copper phthalocyanine (0.0024 mole) recoverable by reduction.

Metal-free phthalocyanine and phthalocyanines of magnesium, zinc, iron, cobalt, and nickel are also reversibly oxidized but perchlorinated copper phthalocyanine is resistant to oxidation.

Phthalocyanines react more readily in the *alpha*-form than in the *beta*-form of crystals.

The relative order of reactivity of the peroxides, estimated by observing the start of the formation of the oxidation products as judged by sight and confirmed by spot-testing with a reducing agent, is: bis(2,4-dichlorobenzoyl) peroxide > bis(4-chlorobenzoyl) peroxide > benzoyl peroxide > lauroyl peroxide > *tertiary*-butyl hydroperoxide. Perbenzoic acid also oxidizes phthalocyanines. Neither anhydrous nor aqueous hydrogen peroxide gave any measurable quantity of the oxidation product.

Ether, acetone and 2-alkoxyethanols are satisfactory solvents for use with peroxides. No advantage is gained by deviating from room temperature.

The oxidation products are stable if protected from reducing agents and hydrolytic conditions. They are brownish solids which do not melt but are converted into phthalocyanines between 140–220°. Any reducing agent will regenerate the phthalocyanines which are always obtained in the *alpha*-form of crystals.

Copper phthalocyanine and chlorine. Five g. of *beta*-copper phthalocyanine (0.0087 mole) were suspended in 100 ml. of anhydrous methanol and stirred while 1.5 g. of chlorine gas (0.021) were passed into the mixture in 5 min. The charge was stirred for 5 min. more and filtered directly into 100 ml. of water containing 10 g. of sodium carbonate (0.095 mole). The precipitate was filtered, washed with water, and dried at 50°. Two and a half g. of yellow powder were obtained.

Anal. It is difficult to assign an exact composition to the oxidation products prepared by this method because they are contaminated by various substances, such as copper oxide and phthalimide, which are insoluble in aqueous sodium carbonate. Found: N, 15.4; Cu, 9.0; Cl, 2.9, copper phthalocyanine by reduction, 72.

Iron phthalocyanine and chlorine. Twenty-two and seven-tenths g. of very finely ground iron phthalocyanine (0.04 mole) were suspended in 360 ml. of anhydrous methanol and stirred vigorously. Six and a quarter g. of chlorine gas (0.088 mole) were passed into the suspension in 5 min. during which period the temperature of the reaction mass rose spontaneously from 24° to 33°. The charge was stirred for 5 min. more and filtered directly into 400 ml. of water containing

40 g. of sodium carbonate (0.38 mole). The precipitate was filtered, washed with dilute aqueous sodium carbonate, and dried in a vacuum oven at 50°. Fourteen and a half g. of yellow powder were obtained.

Anal. As in the previous example and for the same reason it is difficult to assign an exact composition to this oxidation product. Found: N, 16.3; Cl, 1.3; Fe, 9.44; iron phthalocyanine by reduction, 87.

Iron phthalocyanine possesses interesting catalytic properties, such as for the decomposition of hydrogen peroxide and organic hydroperoxides and for the autoxidation of many substances. Dispersion of iron phthalocyanine on different supports can be prepared conveniently by treating the supports with a solution of the above product and depositing the phthalocyanine *in situ* by reduction with, for example, ascorbic acid.

Copper phthalocyanine and tertiary-butyl hypochlorite. Fifty g. of *alpha*-copper phthalocyanine (0.087 mole) were vigorously agitated with 24 g. of *t*-butyl hypochlorite (0.221 mole) in one liter of anhydrous methanol at 25° for 70 min. The reaction mass was filtered and the filtrate was allowed to stand at room temperature for 3 days. Dark, reddish brown transparent crystals, consisting of stout needles pointed at both ends and measuring up to 600 by 40 μ , deposited during this period. They were removed by filtration, washed with methanol and dried at 82°. Three and fifty-five-hundredths g. of crystals were recovered.

Anal. Calcd. for III, R = *t*-butyl (Fig. 3), $C_{36}H_{26}ClCuN_8O$: N, 16.36; Cu, 9.28; Cl, 5.18, copper phthalocyanine by reduction, 84.1. Found: N, 16.98; Cu, 9.48; Cl, 5.26, copper phthalocyanine 75.

Reduction of the product dissolved in 2-methoxyethanol with titanium trichloride, hydriodic acid or hydrogenation showed that two equivalents of reducing agents are required to produce a mole of copper phthalocyanine. Chlorine is evolved when these crystals are treated with either concentrated sulfuric acid or aqueous hydrochloric acid.

An identical oxidation product was obtained by treating *beta*-copper phthalocyanine in the same way.

Zinc $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine and benzoyl peroxide. Thiophene-free benzene solution of the porphine containing 0.00197 g. per liter is a purple solution which gave spectrum of Fig. 8, solid line. To this solution was added 0.00198 g. of benzoyl peroxide. After standing at 24–27° for 20 hr. in the dark, this solution had become yellow and gave spectrum of Fig. 8, dashed line. The optical density at 425m μ had dropped from 1.00 to 0.34, and that at 550m μ from 0.041 to 0.017. On the other hand, new weak peaks had developed at 450m μ and 645m μ . Twenty ml. of the oxidized solution were mixed with 5 ml. of methanol saturated with ascorbic acid, allowed to remain at 24–27° for 20 hr. in the dark, and washed with water to remove the methanol and excess ascorbic acid. The dried benzene solution was purple again and gave a spectrum similar to Fig. 8, solid line except that the optical density at 425m μ was 0.89 instead of 1.00. The oxidized solution did not regenerate a purple solution on treatment with ascorbic acid when it had aged for 3 days.

The optical density at 425m μ was reduced to 0.08 in 20 hr. when the concentration of benzoyl peroxide was increased to 220×10^{-6} mole, and a definite peak was developed at 450m μ (optical density: 0.09).

It was found that *t*-butyl hydroperoxide and α -cumyl hydroperoxide also oxidize the porphine but very much more slowly than benzoyl peroxide.

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