According to the Nernst equation

$$E = E^0 - (RT/nF)\{\ln([H_3AsO_4]/[H_3AsO_3]) - \ln[(a_{H^+})^2/(a_{H_2O})]\} \quad (19)$$

Foerster and Pressprich assumed that the only effect to be considered in the calculation of the potentials was the variation in hydrogen ion activity, since the ratio of $[H_3AsO_4]$ to $[H_3AsO_3]$ was kept equal to unity. However, the present work has shown that the concentrations of arsenious acid and therefore the potentials at various hydrochloric acid concentrations can be calculated only by applying the equilibrium constants found above. The results of such a series of calculations are shown in Table III and are compared with the experimental values found by Foerster and Pressprich. The half-cell value of −0.559 v. given by Latimer[24] was used.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED POTENTIALS

The observed half-cell potentials are those measured by Foerster and Pressprich.[7] The calculated potentials are based on the assumption 1, above.

HCl (*VF*)	E_{obsd}, v.	E_{calcd}, v.
1	−0.580	−0.559
2	− .601	− .597
4	− .641	− .643
6	− .703	− .696
8	− .808	− .756

It is seen that the calculated and observed values agree reasonably well except in 1 and 8 *VF* solutions. Since the reaction between arsenic acid and iodide in 1 *VF* hydrochloric acid is slow, the potential of that system may have been measured before equilibrium was attained, thus giving the high result. The concentration of arsenious acid in 8 *VF* hydrochloric acid is very low; a small error in its value could cause a large error in the value of the calculated potential. Such an error is quite possible in view of the uncertainty in the calculated constants and may well account for the discrepancy between the calculated and measured potentials in 8 *VF* hydrochloric acid.

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One-Equivalent Intermediates in Phthalocyanine and Porphin Oxidations Investigated by Paramagnetic Resonance

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The paramagnetic resonance absorption technique has been used to show that the two-equivalent oxidation of both metal-free phthalocyanine and $\alpha,\beta,\gamma,\delta$-tetraphenylporphin proceed *via* a one-equivalent oxidation intermediate, with properties very similar to those of the more stable intermediates formed from the Cu^{II}, Co^{II} and Al^{III} phthalocyanines. All the intermediates are paramagnetic and have a *g*-value extremely close to the free-spin value, but the line width varies from one intermediate to another. The data are in accord with a postulated structure, common to all the intermediates, in which the macrocyclic ring remains intact and the unpaired electron is situated in a π-orbital.

Introduction

Dent, Linstead and Lowe[2] first investigated the oxidation of metal phthalocyanine complexes by ceric sulfate, using suspensions in dilute sulfuric acid, and showed a two-equivalent reaction to occur giving colorless products according to equation 1.

$$(C_8H_4N_2)_4Cu + 8H_2O + 4H^+ \longrightarrow Cu^{2+} + 4C_8H_5O_2N + 4NH_4^+ + 2e^- \quad (1)$$

A reddish-purple intermediate was observed when *two equivalents* of Ce^{IV} reacted at 0° with suspensions of the metal-free phthalocyanine, metal-free tetrabenztriazaporphin and its copper complex, followed in the two latter cases by a slower further oxidation corresponding to the uptake of five oxygen atoms.[3,4] However, using the water-soluble tetrasulfonated metal phthalocyanine complexes, Cahill and Taube[5] identified the reddish-purple intermediate as a *one-equivalent* oxidation product by spectrophotometric titration with 0.5, 1.0 and 2.0 moles Ce^{IV} per mole of phthalocyanine. In the previous experiments[3,4] an excess of Ce^{IV} was always used, and the discrepancy between the two sets of results may be connected with inhomogeneous oxidation occurring in the suspensions. An identical intermediate was obtained with the Cu^{II}, Co^{II}, Zn^{II}, Al^{III} and Fe^{III} complexes, the particular metal only affecting its rate of production and its rate of disproportionation and further oxidation, as represented by equations 2, 3 and 4,

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where TSCP stands for tetrasulfonated copper phthalocyanine.[5]

$$\text{TSCP} + \text{Ce}^{\text{IV}} \longrightarrow \text{TSCP}^{+} + \text{Ce}^{\text{III}} \quad (2)$$

$$2\text{TSCP}^{+} \longrightarrow \text{TSCP} + \text{stable, colorless products} \quad (3)$$

$$\text{TSCP}^{+} + \text{Ce}^{\text{IV}} \longrightarrow \text{Ce}^{\text{III}} + \text{stable, colorless products} \quad (4)$$

The stability of TSCP$^+$, unlike the intermediates from the other metal complexes, was much greater in sirupy phosphoric acid as solvent, with a half-life of about four hours at 2°. These equations imply that the metal is still bound in the intermediate, and this was confirmed by reduction, which gave a product with a spectrum identical to that of the original metal complex. Cahill and Taube[5] proposed that the intermediate is a higher oxidation state of the metal complex, formed by electron removal from a π-orbital of the conjugated ring system. Other strong oxidizing agents, with E_0 above about 1.0 volt gave similar results, and still more were found effective by George,[6] who compared this one-equivalent oxidation with those occurring in hemoprotein systems.

Metal porphyrins possessing methine C–H groups which include all the naturally occurring porphyrins, are very susceptible to oxidative attack leading to ring fission,[7] and, with the possible exception of the compound that iron uroporphyrin forms with peroxides in alkaline solution,[6,8] there is no evidence for the formation of higher oxidation states of the metal complexes. However, with the metal free $\alpha,\beta,\gamma,\delta$-tetraphenylporphin, where the methine H-atoms are replaced by phenyl groups, George and Goldstein[9] found oxidation by ceric salts and the other strong oxidizing agents to yield a stable two equivalent oxidation product which could be reduced quantitatively back to the original porphin. In this oxidation, carried out in sirupy phosphoric acid, the color change is from green to an orange-brown, but appears dull violet in the early stages indicative of a transient one-equivalent intermediate. Linstead and Weiss[4] observed brown oxidation products from suspensions of tetrabenzporphin and tetrabenzmonoazaporphin, and although the over-all reaction taking 12 hours involved the equivalent of nine oxygen atoms, the brown color suggests that a similar two-equivalent oxidation may occur initially.

Cahill and Taube[5] noted that the oxidation of metal-free sulfonated phthalocyanine solutions, unlike that of phthalocyanine suspensions,[4] proceeded rapidly giving colorless products with no noticeable formation of an intermediate: repeating this experiment we found the blue-green solution to darken somewhat at first, indicating that a very transient intermediate may be present in this system too.

Single equivalent oxidation intermediates of porphins, phthalocyanines and the diamagnetic metal phthalocyanine complexes would possess an unpaired electron. Those of the paramagnetic metal phthalocyanine complexes would correspondingly have an additional unpaired electron. Their presence should be detected readily by paramagnetic resonance, and we have therefore studied the oxidation reactions using this technique to see whether transient intermediates are actually formed from the metal-free compounds, and to gain further information on the electronic structure of the relatively stable intermediates from the metal phthalocyanines.

Experimental

Sulfonated metal-free phthalocyanine was kindly supplied by Imperial Chemical Industries, Ltd. Professor H. Taube generously provided samples of aluminum and cobalt phthalocyanine and the tetrasulfonated copper derivative used in his original investigations,[5] which had been supplied through the courtesy of Dr. N. M. Bigelow, Jackson Laboratory, E. I. du Pont de Nemours and Co. The $\alpha,\beta,\gamma,\delta$-tetraphenylporphin, synthesized by the method of Rothemund and Menotti,[10] was kindly provided by Mr. J. M. Goldstein. It had been purified chromatographically using alumina and then "Magnesol" (talc) columns. The infrared absorption spectrum was then determined and found to be identical with that reported by Thomas and Martell,[11] showing the sample to be of high purity and free from chlorins and porphin-type impurities. The phthalocyanines were used without further purification. A previous analysis of the tetrasulfonated copper derivative showed it to be 85% pure, the main contaminants being inorganic salts introduced during its preparation.[5] Control experiments showed that typical impurities, chlorides and sulfates, had no effect on the oxidation behavior.[5] No similar purification procedure is available for the phthalocyanines, and probably the aluminum and cobalt compounds were as impure as the copper compound. The correspondence between the changes in optical spectra and the changes in paramagnetic resonance absorption spectra described below, as oxidation proceeds first to one equivalent and then to two equivalent oxidation products, leaves little doubt that the transient intermediate with a g-value of 2 is the radical intermediate of the phthalocyanine, and not a radical species formed from impurities.

Very concentrated aqueous solutions of the water-soluble sulfonated derivatives were used, 10^{-3}–10^{-2} M, acidified with a little concentrated sulfuric acid. The aluminum and cobalt phthalocyanines and the tetraphenylporphin were dissolved in sirupy phosphoric acid: concentrated sulfuric acid was an equally effective solvent, but was only employed for the two metal phthalocyanines.

Paramagnetic resonance absorption measurements were made at both 1.25 cm. and 8 mm. wave lengths, and standard crystal-video methods of detection and display were used in both cases. Low temperature resonators[12] incorporating nickel–silver wave guide feed were employed, and the solutions to be investigated were placed in a shallow circular Distrene cup, placed centrally at the bottom of the H_{111} cylindrical cavity. The signals obtained from the intermediate oxidation products were very similar to those obtained from free radicals trapped in low temperature carbons,[13] and all but one had widths of about 10 gauss, with g-values very close to the free-spin values. They could therefore be observed as sharp absorption lines on the oscilloscope screen when normal field modulations of 200 gauss were used, and their g-values could be measured very accurately by direct comparison with the absorption of a small quantity of hydrazyl placed on the solution. The magnetic fields were measured by a proton resonance meter, and its signal was displayed simultaneously with the microwave signal on the same oscilloscope screen.

The solution of the particular phthalocyanine or porphin was made up and tested in the spectroscope as a blank, no signal being obtained from the metal-free or diamagnetic

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metal derivatives. Ceric ammonium nitrate was then added, the solution stirred, and, after tuning the cavity for resonance, the whole resonator was quickly cooled to 90°K. in liquid oxygen. Photographs of the signal obtained were then taken, and, after warming to room temperature for a few minutes to allow oxidation to continue, the procedure was repeated thus enabling the progress of the reaction to be followed.

Results

(a) **Metal-free Sulfonated Phthalocyanine, and $\alpha,\beta,\gamma,\delta$-Tetraphenylporphin.**—In both cases direct evidence was obtained for the presence of a transient free-radical intermediate. The initial solutions gave no absorption when tried as blanks, but after addition of the ceric ammonium nitrate, intense signals were observed with identical line widths of 10 gauss and g-values of 2.0024. The signal was observed to decrease and finally disappear as oxidation was allowed to proceed giving the colorless products in the case of the phthalocyanine, and the stable orange-brown product in the case of the porphin. This confirms that the signal is due to an intermediate oxidation product, and, on the basis of the chemical evidence which shows both over-all reactions to be two-equivalent processes,[2,9] the intermediate is identified as the transient one-equivalent oxidation state in these particular reactions. The macrocyclic ring must be intact in the porphin intermediate since reduction of the two-equivalent oxidation product regenerates the porphin quantitatively. By analogy, the ring is probably intact in the phthalocyanine intermediate, with ring fission occurring as a consequence of the second oxidation step. This is certainly the case with the metal phthalocyanines, since Cahill and Taube[5] showed that reduction of the one-equivalent oxidation product gave complete recovery of the original complex.

(b) **Aluminum and Cobalt Phthalocyanine, and Copper Tetra-sulfonated Phthalocyanine.**—The far more stable intermediates from these three metal complexes all gave well defined signals. As before, the absorption near the free-spin value decreased and finally disappeared as the oxidation went to completion, confirming that it is associated with the presence of the intermediate. The line widths and g-values, calculated by comparison with the hydrazyl signal, are listed in Table I with those for the metal-free compounds. The g-values are identical within experimental error, whereas the line width varies from one intermediate to another, and is especially broad for the intermediate from the copper complex.

Table I

Paramagnetic Resonance Absorption Data for One-equivalent Oxidation Intermediates of Porphin and Phthalocyanine Derivatives

Parent compd.	g-Value	Line width, gauss
$\alpha,\beta,\gamma,\delta$-Tetraphenylporphin (metal free)	2.0024 ± 0.0002	10
Sulfonated phthalocyanine (metal free)	2.0024 ± .0002	10
Aluminum phthalocyanine	2.0024 ± .0002	6
Cobalt phthalocyanine	2.0024 ± .0002	6
Copper tetra-sulfonated phthalocyanine	2.002 ± .001	85

With the cobalt and copper derivatives it was necessary to differentiate between the absorption due to the intermediate, the original metal complex, and the final oxidation product. Fortunately both cobalt and copper salts have paramagnetic absorption spectra which are fairly well removed from $g = 2.0$, typical values being $g_{\perp} = 2.5$–3.0, $g_{\parallel} = 5.5$–7.0 and $g_{\perp} = 2.1$, $g_{\parallel} = 2.4$, respectively,[14] hence the free radical absorption produced by the intermediate is not obscured by the normal signals. The progress of the oxidation of the tetrasulfonated copper phthalocyanine is illustrated in Fig. 1. Here the different absorption spectra obtained from the same solution as oxidation by ceric ammonium nitrate proceeds are placed underneath each other in chronological order, the last spectrum being that of the products when the reaction has ceased. A similar sequence was obtained with cobalt phthalocyanine, but in this case the signal due to the intermediate was more readily identifiable by reason of its smaller width, 6 gauss as compared to 85 gauss, giving a much sharper absorption line.

In the case of these intermediates from paramagnetic metal complexes further experiments will be required to determine the additional g-values characteristic of the metal in the intermediate. In the present experiments it is possible that the partially oxidized solution contained some metal phthalocyanine which had not reacted, and, judging from Fig. 1, a considerable quantity of the fully oxidized products. A further complication is that in the concentrated solutions which have to be used, the disproportionation reaction 3 is favored, regenerating the original metal phthalocyanine.

Discussion

These experiments have shown that in the two-equivalent oxidation of both the metal-free $\alpha,\beta,\gamma,\delta$-tetraphenylporphin and phthalocyanine a one-equivalent intermediate participates with properties very similar to those of the more stable intermediates formed in the corresponding oxidation of the Cu^{II}, Co^{II} and Al^{III} phthalocyanines. All the intermediates are paramagnetic and have a g-value extremely close to the free-spin value. This shows that there is very little coupling between the unpaired electron and any orbital momentum, which would be in keeping with the suggestion of Cahill and Taube,[5] with regard to the metal complex intermediates, that the odd electron is associated with a π-orbital of the ring system rather than with the central metal atom. Additional support for this kind of electronic structure lies in the narrowness of the absorption lines for the intermediates from the metal-free compounds and the aluminum and cobalt phthalocyanine, although the much broader line for the intermediate from the copper phthalocyanine is difficult to account for, and more work may be necessary to understand its origin. The absence of hyperfine structure provides further support. It is very unlikely that hyperfine structure is actually present and obscured with the concentrated solutions employed, since it has been observed using crystalline samples of copper porphin

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derivatives where the copper concentration is much higher.[15]

The production of a one-equivalent oxidation intermediate from the metal complexes, with the requisite physical and chemical properties, is restricted to an electron removal process. The alternative, the removal of a hydrogen atom, can be ruled out for the following reason. The only H-atoms in the metal phthalocyanine structure are those of the benzene rings, so the isolation of phthalimide in almost quantitative yield in the final oxidation products[2] shows that these H-atoms are resistant to oxidative attack. In the case of the metal-free derivatives, however, there is the possibility that one of the H-atoms on two of the pyrrole rings are involved. The existence of a stable two-equivalent oxidation product from the $\alpha,\beta,\gamma,\delta$-tetraphenylporphin favors this hypothesis, for a reasonable mechanism for its formation entails the removal of these two H-atoms and the introduction of a new double bond into the conjugated ring system.[9] Hence the intermediates from the metal-free compounds and from the metal complexes may differ structurally in being formed by H-atom and electron removal, respectively; however, both types of radical structure would be characterized by an electron in a non-localized orbital giving very similar g-values and line widths. Nevertheless, the difference might be one of mechanism only, because, in the acid medium used, any tertiary N-atoms formally present very probably would be combined with protons giving cationic forms of the intermediates like those of the parent porphin and phthalocyanine.[16]

Finally, it is of interest to compare the present results with those obtained in the pyrolysis of phthalocyanine derivatives. Previous work[17] has shown that all diamagnetic phthalocyanine derivatives give intense free radical absorption when charred at about 450°. This absorption also has a line width of about 10 gauss, and detailed measurement has shown that the width is dependent to some extent on the diamagnetic metal present.[18] Similar absorption has been observed in any carbon formed by pyrolysis at temperatures below 500°.[13] The trapped free radicals have been identified with trivalent carbon centers resulting from the fission of ring structures in the solid compound. It would thus appear that in the pyrolysis of a phthalocyanine the ring structure is permanently disordered, an unpaired electron is completely trapped, and, as a consequence, the free radical is very stable. On the other hand when oxidation occurs in solution, although a free radical is formed initially it is of a different kind. The macrocylic ring remains intact and the unpaired electron is in a π-orbital of the conjugated system. The stability of the free radical depends in this case on the rate of the disproportionation reaction that can occur by collision in solution, and on the likelihood of further oxidation converting the radical into a two-equivalent oxidation product.

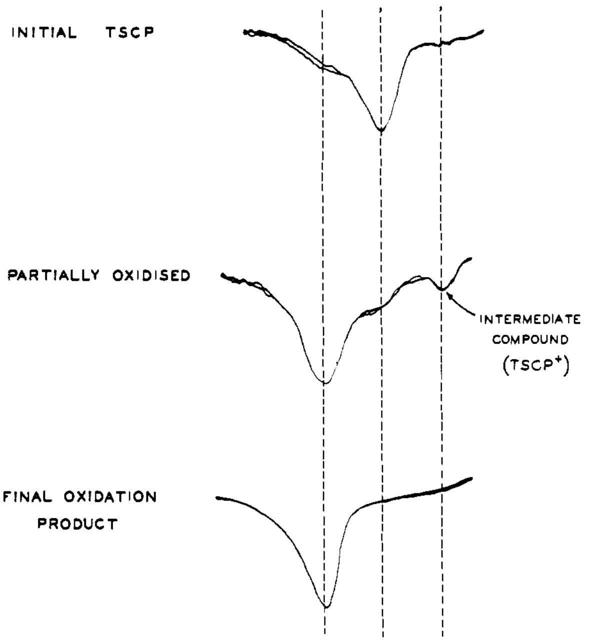

Fig. 1.—Absorption changes throughout the oxidation of tetra-sulfonated copper phthalocyanine, showing the decay of the copper phthalocyanine peak, the appearance of the peak due to the cupric salt formed, and the small peak (at the right-hand side of the center spectrum) characteristic of the intermediate. Measurements taken at 1.25 cm. wave length and 90°K.

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