[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Effect of X-Rays and β-Irradiation on $\alpha,\beta,\gamma,\delta$-Tetraphenylporphine. I. Sirupy Phosphoric Acid, Concentrated Sulfuric Acid and 49% Sulfuric Acid as Solvents[1]

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The action of 118 kv. X-rays and β-particles on $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (TPP) has been studied. The changes occurring on irradiation of TPP in sirupy phosphoric acid, concentrated sulfuric acid and 49% sulfuric acid were followed spectrophotometrically and were found to correspond to one and two electron oxidation states of TPP. The spectra were proven to be qualitatively identical to those produced by the Fenton reaction and ceric ions. The spectrophotometric titrations with ceric ions showed one and two electron oxidations to be involved. The oxidation, whether produced by irradiation or by chemical oxidizing agents, was quantitatively reversed by the addition of ferrous sulfate immediately after oxidation. A more gradual regeneration of the original TPP from both oxidation states in the absence of added reducing agents suggested the disproportionation of oxidized TPP into free TPP and some higher oxidation states from which the original TPP could not be regenerated. A linear relationship was found between irradiation dose and the decrease in optical density of the Soret band up to about 1000 r. A 50% decrease in the Soret band resulted after X-irradiation with approximately 620 r. in sirupy phosphoric acid.

Introduction.—The chemical and physical properties of tetraphenylporphines have been studied by various investigators,[2–15] but no work has been reported on the effects of irradiations on this compound. The purpose of this paper is to present our observations on the effects produced by X- and β-rays on tetraphenylporphine in inorganic acids. This substance when dissolved in acidic media acquires a green color with highly specific absorption spectra and the effects produced by ionizing radiations may be investigated by spectrophotometric measurements.

Materials.—Tetraphenylporphine was synthesized in this Laboratory by the method of Ball, Dorough and Calvin,[3] and purified chromatographically by the method of Priesthoff and Banks[9] using activated alumina and Magnesol as adsorbents (kindly supplied by Westvaco Chemicals, S. Charleston, W. Va.).

The infrared spectrum of the purified material agreed with that obtained by Thomas and Martell.[13]

P^{32}, commercial P-labeled phosphoric acid manufactured by ORNL Union Carbide Nuclear Co., was used as the source of β-particles.

Methods.—All X-irradiations were performed in an open vessel, 3.5 cm. in diameter with solutions equilibrated with the air using a Picker X-Ray Corporation machine operated at 118 kV. and 10 mA. The vessel containing 10 ml. of solution was placed 19 cm. from the X-ray tube and irradiated at the rate 488 r. per minute, as determined with the aid of a 100 r. Victoreen chamber. Complete visible spectra were obtained on the products after each irradiation.

All spectrophotometric measurements were made with the model DU Beckman spectrophotometer. Photometric titrations were performed at the Soret band, 540 and 700 mμ on 25-ml. portions of the standard TPP solution using ceric sulfate as titrant. After addition of each increment of the titrant, and mixing, enough solution was withdrawn for photometric measurements. In addition, the complete spectra were determined at various stages of the titration over the range from 400 to 720 mμ.

The infrared spectrum was obtained on the Perkin-Elmer, model 21 C, double beam, recording spectrophotometer, using the potassium bromide disk technique.

Results and Discussion

Tetraphenylporphine in Sirupy Phosphoric Acid.—On X-irradiation of tetraphenylporphine in sirupy phosphoric acid there was a decrease of the Soret band at 437 mμ and of the band at 660 mμ. Formation of bands were observed at about 460 and 540 mμ, and a broad band at 660 to 710 mμ (Figs. 1 and 2). The last band consists probably of two over-lapping bands, with the original at 660 mμ, and a new band with the center at approximately 700 mμ.

Up to an irradiation dose of about 1000 r. there was observed a linear decrease in the optical density of the Soret band. No relation between irradiation dose and optical density of the Soret band was observed at radiation doses of 1000 to 5000 r. A 50% decrease in the Soret band resulted after X-irradiation with approximately 620 r. (Fig. 3). The same linear relationship was observed between the optical density at 540 mμ and irradiation dose. A plot of these quantities yields two straight lines which intersect at approximately 620 r. (Fig. 3).

Identical changes in the absorption spectrum were produced when tetraphenylporphine in sirupy phosphoric acid interacted with 0.690 Mev. β-particles from the P^{32} source (Figs. 1 and 2).

Figures 1 and 2 compare the spectra of the products obtained after irradiation of tetraphenylporphine with the spectra resulting from the addition of the oxidizing agents, ceric ion and Fenton reagent, to tetraphenylprophine. The spectra are essentially identical.

George and Goldstein[14] found with tetraphenylporphine in sirupy phosphoric acid many strong oxidizing agents yield a stable higher oxidation state, and the preliminary spectrophotometric titrations of tetraphenylporphine with ceric ions

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[1] Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, New York, N. Y., September, 1957.

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[13] D. W. Thomas and A. E. Martell, THIS JOURNAL, **78**, 1335 (1956); **78**, 1338 (1956).

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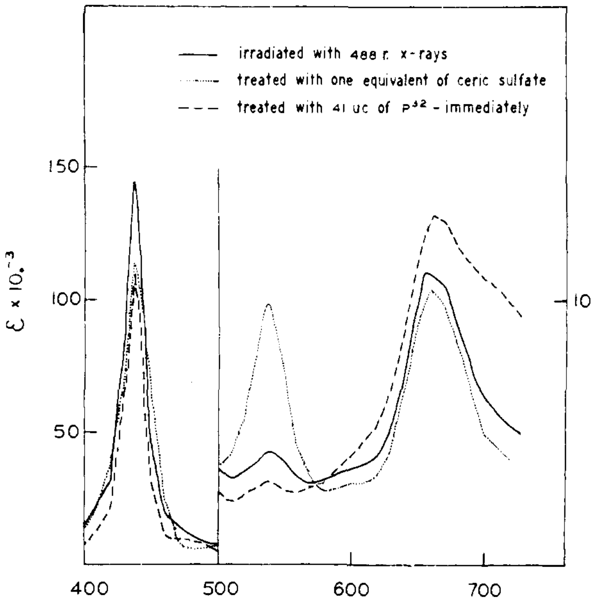

Fig. 1.—Effect of X-rays, β-irradiation and ceric ions on the absorption spectra of tetraphenylporphine in sirupy phosphoric acid.

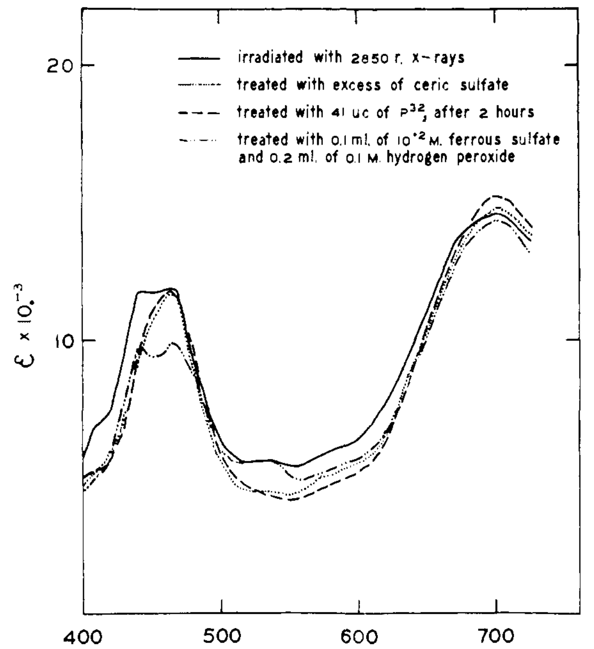

Fig. 2.—Effect of X-rays, β-irradiation, Fenton reagent and ceric ions on the absorption spectra of tetraphenylporphine in sirupy phosphoric acid.

showed two equivalents to be involved. The spectrophotometric titrations performed in connection with this study confirmed the preliminary titration results of George and Goldstein. In addition we found a definite indication of a one electron oxidation state (Fig. 4) which lies within 10% of the theoretical value. The absorption peak at 540 mμ was found to be produced in case of the one electron oxidation state only and reached the

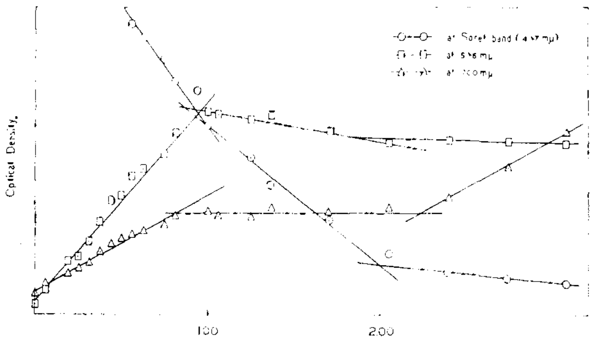

Fig. 3.– Photometric titration of tetraphenylporphine with ceric sulfate.

maximum when one equivalent of ceric ions had been added. The disappearance of this peak was accompanied with the formation of the two electron oxidation state of tetraphenylporphine. The results of the titrations performed on solutions of different concentrations agree within 5%.

The addition of reducing agents to the oxidized product regenerated tetraphenylporphine quantitatively when the addition occurred immediately after oxidation. This was found to be true irrespective of the way the oxidation was induced. Two equivalents of ferrous sulfate was required to reduce the oxidized product of tetraphenylporphine. Titration curves do not show the formation of one electron oxidation state during the reduction process.

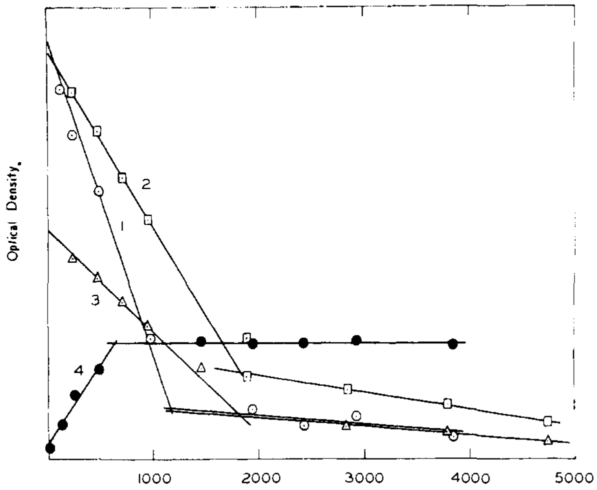

Fig. 4.—Relationship between optical density of absorption bands of tetraphenylporphine and irradiation dose: 1, Soret band in sirupy phosphoric acid; 2, Soret band in concentrated sulfuric acid; 3, Soret band in 49% sulfuric acid; 4, 540 mμ band in sirupy phosphoric acid.

George and Goldstein[14] concluded that the oxidation products were stable, and our experiments confirmed this when an excess of oxidizing agent was present. In the absence of excess oxidizing agent the spectra of the oxidation products changed with time at room temperature (Fig. 5). This behavior was found to take place in all products, no matter what agent was used for oxidation. Irradiated solutions showed an increase in the peak at the Soret band and decreases of the peaks at 470,

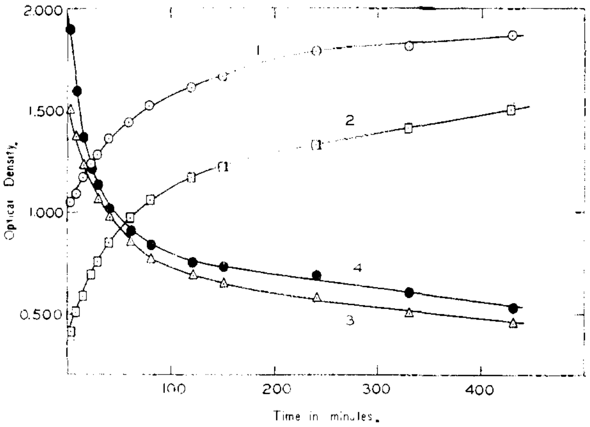

Fig. 5.—Changes with time of the optical density of absorption bands of oxidized tetraphenylporphine in sirupy phosphoric acid: 1, Soret band of TPP oxidized with approximately one equivalent of ceric sulfate; 2, Soret band of TPP oxidized with approximately two equivalents of ceric sulfate; 3, 540 mμ band of TPP oxidized with approximately one equivalent of ceric sulfate; 4, 540 mμ band of TPP oxidized with approximately two equivalents of ceric sulfate.

540 and 700 mμ. The absorption spectra of the solutions treated with approximately one and two equivalents of ceric ions after 5 days acquired all characteristics of the spectra of tetraphenylporphine. These results might be explained by assuming that disproportionation, similar to that suggested by Cahill and Taube,[16] for one electron oxidized tetrasulfonated copper phthalocyanine, takes place. Possible reactions are

$$\mathrm{TPP} + \mathrm{Ce}^{4+} \longrightarrow \mathrm{TPP}^{+} + \mathrm{Ce}^{3+} \qquad (1)$$

$$\mathrm{TPP}^{+} + \mathrm{Ce}^{4+} \longrightarrow \mathrm{TPP}^{2+} + \mathrm{Ce}^{3+} \qquad (2)$$

$$\mathrm{TPP}^{2+} + n\,\mathrm{Ce}^{4+} \longrightarrow n\,\mathrm{Ce}^{3+} + \text{stable, higher oxid. prod.} \qquad (3)$$

$$2\mathrm{TPP}^{+} \longrightarrow \mathrm{TPP} + \text{stable, higher oxidation products} \qquad (4)$$

$$2\mathrm{TPP}^{2+} \longrightarrow \mathrm{TPP} + \text{stable, higher oxidation products} \qquad (5)$$

No indication was found of the reaction

$$2\mathrm{TPP}^{2+} \longrightarrow \mathrm{TPP}^{+} + \text{stable, higher oxidation prod.} \qquad (6)$$

In this case the formation of a peak at 540 mμ would have been noted.

The existence of the one electron oxidation state also has been proved without doubt by George, Ingram and Bennett[15] using the paramagnetic resonance absorption technique.

Tetraphenylporphine in Concentrated Sulfuric Acid and 49% Sulfuric Acid.—The dissolution of tetraphenylporphine in concentrated sulfuric acid is accompanied by sulfonation of the phenyl rings.[8] The absorption spectrum of tetraphenylporphine in concentrated sulfuric acid was found to be practically identical with the spectrum obtained by Menotti[8] for the sulfonated material. On the other hand, Dorough, Miller and Huennekens[4] show a spectrum which is quite different from both spectra mentioned above. The closer inspection of this spectrum[4] reveals that it is a spectrum of an oxidation product of tetraphenylporphine in concentrated sulfuric acid. The decreased Soret band, a new peak at approximately 540 mμ, and indication of the formation of a new peak at 700 mμ showed a great similarity with the spectra of oxidation products in sirupy phosphoric acid. A closer investigation of this problem showed that tetraphenylporphine immediately after solvation with concentrated sulfuric acid acquired a brownish color. This solution produced the spectrum with the similar pattern to that shown by Dorough, Miller and Huennekens.[4] On standing, or after addition of a reducing agent (ferrous sulfate), the spectrum changed to that found by Menotti[8] for sulfonated material alone. On dissolving in concentrated sulfuric acid, it may be suggested that the tetraphenylporphine is oxidized. The oxidation product undergoes reduction on addition of ferrous sulfate, regenerating free tetraphenylporphine (or rather sulfonated tetraphenylporphine). Alternatively, disproportionation to free tetraphenylporphine (sulfonated tetraphenylporphine) and some higher oxidation products takes place on standing as postulated for the oxidation products of tetraphenylporphine in sirupy phosphoric acid.

The effects of X-rays on tetraphenylporphine in concentrated sulfuric acid were found to be qualitatively identical with those obtained for tetraphenylporphine in sirupy phosphoric acid. The inspection of the spectra of the irradiated species revealed that the decrease of the Soret band and the formation of new bands at approximately 470 and 700 mμ could be interpreted as the formation of oxidation products of tetraphenylporphine. A linear relationship between the optical density of the Soret band and radiation dose was found for this system up to the dose of approximately 1850 r. (Fig. 3).

β-Particles, Fenton reagent and ceric ions upon interaction with tetraphenylporphine in concentrated sulfuric acid formed, as expected, oxidation products with spectra identical with those obtained after X-irradiation.

The rate of disproportionation of the oxidation products of tetraphenylporphine was found to be much more rapid in sulfuric acid than in phosphoric acid.

Tetraphenylporphine in concentrated sulfuric acid and in 49% sulfuric acid was found to be less sensitive toward ionizing radiations than in sirupy phosphoric acid. A 50% decrease in the Soret band was produced in both concentrated sulfuric acid and 49% sulfuric acid upon X-irradiation with approximately 1150 r. as compared to 620 r. in the case of phosphoric acid. This would indicate that the sensitivity toward irradiations changes with the medium in which the irradiation is performed.

A possible mechanism of oxidation by irradiations may involve radicals which are formed on irradiation of the solvent, *e.g.*, hydroxyl radicals.[17-19] Indeed, it has been found that Fenton reagent caused spectral changes of tetraphenylporphine in sirupy phosphoric acid and sulfuric

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acid which were identical with those obtained by X-rays and β-particles.

In addition, formation of other oxidizing species has been postulated upon irradiation of concentrated sulfuric acid and concentrated phosphoric acid. For example, Daniels and collaborators[20] found small quantities of peroxymono- and peroxydisulfuric acids. Since the yield of those peroxyacids is very low, we believe that the contribution to the oxidation of tetraphenylporphine as compared to that due to hydroxyl and perhydroxyl radicals will be only a small fraction.

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The Acidity Function, H_0, and Ion-pair Association Constants in Acetic Acid–Water Mixtures

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The acidity function has been determined for perchloric acid in acetic acid–water mixtures. The data allow the calculation of H_0 for solutions between 0.015 and 0.300 M in perchloric acid for any acetic acid–water mixture having from 10–95% acetic acid by weight. The ion-pair association constants for sodium perchlorate in 95 and 91% acetic acid have been determined using conductometric data. The values of K_a are 1900 and 220, respectively.

In connection with current studies of the mechanisms of chromic acid oxidation in acetic acid–water mixtures it became necessary to obtain data on the effect of the medium on the protonating power of an acid, which may be described by the Hammett acidity function, H_0.[1] It also was desired to have some idea of the magnitude of the ion-pair association constants in these solutions. These quantities have been measured and the results are given below.

The acidity function was measured in the usual fashion, that of determining spectrophotometrically the ratio of conjugate acid to the base using a colored base. For 95 and 91% acetic acid, *o*-nitroaniline was used, and for the other solvent mixtures, and also the lower acid concentrations in 91% acetic acid, *p*-nitroaniline was used. The value 0.99 was taken as the pK_a of *p*-nitroaniline[1] and in order to obtain consistent results in 91% acetic acid, the value −0.57 was taken as the pK_a of *o*-nitroaniline.

Since the values obtained were to be used in connection with kinetic studies, the formal ionic strength of the solution was maintained constant (0.300 M) by the addition of sodium perchlorate. Thus the H_0 values measured here are not exactly comparable to those usually obtained. Perchloric acid was taken as the acid since it is a monobasic acid and appears to be completely ionized (although largely in the form of ion pairs) in glacial acetic acid.[2] The results are given in Table I, and a plot of $-\log [H^+]$ against H_0 is given in Fig. 1.

TABLE I

ACIDITY FUNCTION FOR PERCHLORIC ACID IN ACETIC ACID–WATER MIXTURES

		H_0						
$[HClO_4]$	$-\log [H^+]$	95%	91%	85%	51%	40%	25%	10%
0.300	0.52	−1.43	−0.84	−0.34	0.61	0.64	0.61	0.53
.225	.65	−1.20	− .66	− .18	.72	.77	.75	.65
.150	.82	−0.96	− .46	.03	.92	.95	.93	.82
.075	1.12	− .71	− .12	.36	1.22	1.25	1.24	1.11
.045	1.35	− .48	.10	.59	1.43	1.46	1.44	1.33
.030	1.52	− .21	.28	.76	1.59	1.60	1.58	1.50
.015	1.82	.11	.54	1.03	1.81	1.79	1.81	1.73

From 10–51% acetic acid, a linear relationship is found with a slope of 1.08, neglecting the point for the lowest acid concentration. This concentration is in error because of the "autoprotolysis" of the acetic acid, which contributes a small additional hydrogen ion concentration. The last point is the only one which would be seriously affected by this effect. If the difference between the acidity predicted from the slope and the amount of acid which was added is assumed to be the contribution from the acetic acid, the "autoprotolysis" constant may be calculated to be 5 ± 1 × 10^{-6} for this range of solvent composition.

In solutions containing a larger proportion of acetic acid, some curvature is noted in the plots, and this becomes particularly noticeable with 95% acetic acid. The average slopes are still close to unity indicating that the difference between H_0 and $-\log [H^+]$ is primarily due to a change in the proton level, and suggesting that the ratio of activity coefficients of the indicator base and its conjugate acid is essentially constant and probably close to unity. Thus, in this case, the acidity function is largely a measure of the activity of hydrogen ions.

The nature of the effect of water concentration on H_0 may be seen in a plot of the average $-\log [H^+] - H_0$ for each solution against the logarithm of the molality of water (Fig. 2). For the range of $\log M_{H_2O}$ from 0.5 to 1.2, an essentially linear relationship is obtained with a slope of 2.1. A simple interpretation would be that the reaction may be represented as

$$H_3O^+\cdot H_2O + B \rightleftharpoons BH^+ + 2H_2O$$

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[1] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 267; F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 1 (1957).

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