

shown for methane and ethane are in the integral neutron dose region for which similar experiments with cyclopropane have shown appreciable radiation damage alterations ( $>10^{13}$  n./cm.<sup>2</sup>),<sup>21</sup> only small effects should be expected for the labeled parent molecules. Gaseous ethane experiments carried out for lower integral neutron doses have considerably more HT and less of C<sub>3</sub> and heavier compounds, but approximately the same amount of parent.<sup>22</sup> Hence, the differences in parent yield

(21) J. K. Lee, B. Musgrave and F. S. Rowland, *Canad. J. Chem.*, **38**, 1756 (1960).

(22) A. Beyerlein and F. S. Rowland, unpublished results.

with phase in Table IV are probably not associated with these integral dose differences.

Similarly, searches for temperature effects in recoil tritium reactions have not shown large effects on the T for H substitution,<sup>5,13</sup> although more extensive experiments are desirable.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DETROIT, DETROIT 21, MICHIGAN, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNSYLVANIA]

## Effects of High Energy Radiations on $\alpha,\beta,\gamma,\delta$ -Tetraphenylporphine. II. Formic Acid, Acetic Acid and Propionic Acid as Solvents

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The stability of porphyrins toward irradiations was studied.  $\alpha,\beta,\gamma,\delta$ -Tetraphenyl porphine was used as a model system. The compound was irradiated in formic acid, acetic acid and propionic acid with 118 kV., 10 ma. X-ray and Co<sup>60</sup> gamma rays and the eventual changes were followed spectrophotometrically. In contrast to the behavior in syrupy phosphoric acid and sulfuric acid, no significant changes were noted on irradiation with low dosages up to approximately 5000 r. The higher dosages produce changes, which were interpreted as destruction of the porphine ring. A mechanism involving one and/or two electron oxidation followed by disproportionation is suggested. Hydroxyl and perhydroxyl radicals as well as hydrogen peroxide and peracids seem to be responsible for the oxidation.

### Introduction

It was shown in a previous paper<sup>1</sup> that tetraphenylporphine in syrupy phosphoric acid or sulfuric acid upon interaction with beta-particles or X-radiation undergoes a one and/or two electron oxidation, depending upon the irradiation dose. Identical changes were found to be produced by ceric ions and Fenton reagent. It was suggested that hydroxyl and perhydroxyl radicals were responsible for the oxidations.

The purpose of this paper is to present some results on the action of radiation on tetraphenylporphine in the organic acids, especially formic acid, acetic acid and propionic acid. All three acids are relatively good solvents for tetraphenylporphine, and the resulting solutions have absorption spectra characteristic of the acid salts. The changes occurring upon irradiation can be followed spectrophotometrically, by observing the intensity of the Soret band, as well as the band in the red region.

### Materials

Tetraphenylporphine was synthesized in this Laboratory by the method of Ball, Dorough and Calvin<sup>2</sup> and purified chromatographically by the method of Priesthoff and Banks<sup>3</sup> using activated alumina and Magnesol as adsorbents. The infrared spectrum of the purified material agreed with that obtained by Thomas and Martell.<sup>4</sup>

(1) A. Szutka, J. F. Hazel and W. M. McNabb, *J. Am. Chem. Soc.*, **80**, 3016 (1958).

(2) R. H. Ball, G. D. Dorough and M. Calvin, *ibid.*, **68**, 2278 (1946).

(3) J. H. Priesthoff and C. V. Banks, *ibid.*, **76**, 937 (1954).

(4) D. W. Thomas and A. E. Martell, *ibid.*, **78**, 1338 (1956).

All acids were reagent grade and were used without further purification.

### Methods

X-Irradiations were performed according to the method outlined in the previous paper,<sup>1</sup> using the same X-ray machine and conditions.

For gamma irradiations a Co<sup>60</sup> source of approximately 1100 curies was used. Ten ml. of solution was placed in a Pyrex test tube, stoppered and irradiated in a stainless steel container at the rate of approximately 630 Kr. per hour.

All spectrophotometric measurements were made with the Model DU Beckman Spectrophotometer.

The infrared spectrum was obtained in the Perkin-Elmer, Model 21 C, double beam, recording spectrophotometer.

### Results

No significant changes in the spectra were noticed upon X-irradiation of tetraphenylporphine in formic acid up to the total dose of 5000 r. On the other hand, it was found upon irradiation with much higher dosages of Co<sup>60</sup> gammas that there was a decrease in the optical density of the Soret band at 436 m $\mu$  and of the band at 660 m $\mu$ . In the beginning the decrease in the optical density was proportional to the time of irradiation, but after approximately 22 minutes the optical density fell sharply (Fig. 1). At increased concentrations of tetraphenylporphine, the slope of the first portion of the curve became steeper for both bands. When the acid concentrations were reduced, the sharp drop occurred earlier. Both bands disappeared completely after 20 minutes of irradiation of tetraphenylporphine in 50% formic acid as compared to 18% decrease of both bands in 90% formic acid. The decrease of the optical density

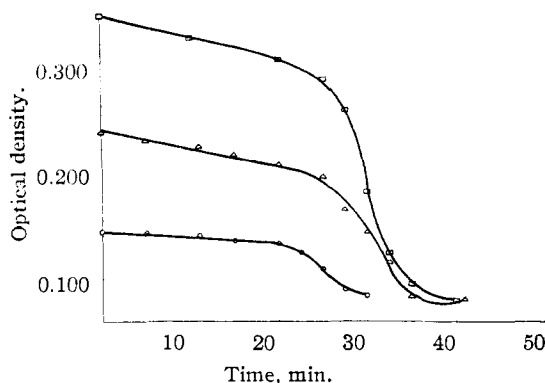


Fig. 1.— $\text{Co}^{60}$  gamma irradiation TPP in 90% formic acid at  $660\text{ m}\mu$ .

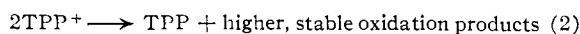
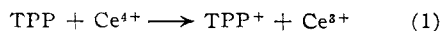
of both bands was found to be irreversible, as judged by the absence of reaction with appropriate reducing agents such as ascorbic acid. The action of ceric ions was similar to that of gamma rays, being marked by a decrease of both bands. The initial formation of a brown compound on addition of ceric ions was similar to that during the one electron oxidation of tetraphenylporphine in syrupy phosphoric acid or sulfuric acid media. The absorption maximum of the brown compound at approximately  $540\text{ m}\mu$  could be observed in a hand spectroscop.

Tetraphenylporphine in acetic acid behaved very much as in formic acid upon X- and gamma-irradiations (Fig. 2). The gradual decrease in the optical density of the Soret band as well as the band at  $655\text{ m}\mu$  was linear with the time of irradiation. It was observed that the destruction of tetraphenylporphine is a function of concentration of tetraphenylporphine and of acetic acid. A rapid decrease in the optical density of both bands occurred after approximately 45 minutes of gamma irradiation.

The action of radiations on the tetraphenylporphine in the third solvent used, propionic acid, did not differ markedly from the two previous solvents, although the sharp drop in both bands occurred after approximately 60 minutes (Fig. 3). Upon interaction with ceric ions, the formation of the metastable one electron oxidized product was observed in all acids.

### Discussion

The spectroscopic study of the products of interaction of ceric ions with tetraphenylporphine in organic acids suggests that a one electron oxidation process takes place. It has been found that this state is metastable and its spectrum changed rapidly to the original spectrum of the tetraphenylporphine. This regeneration of the original spectrum accompanied with the decrease in the Soret band and in the band in the red region is interpreted as disproportionation, analogous to that in phosphoric acid medium.<sup>1</sup> The possible reactions are



Since the two electron oxidation products and higher stable oxidation products do not show any

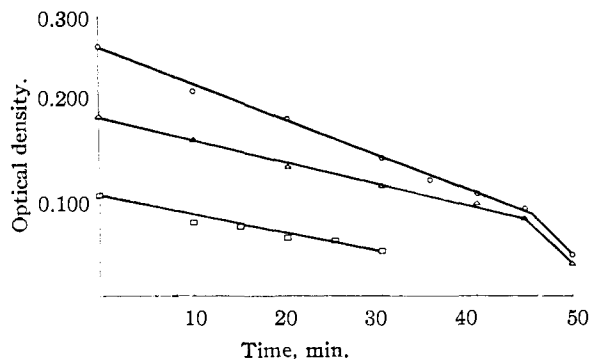


Fig. 2.— $\text{Co}^{60}$  gamma irradiation TPP in 90% acetic acid at  $655\text{ m}\mu$ .

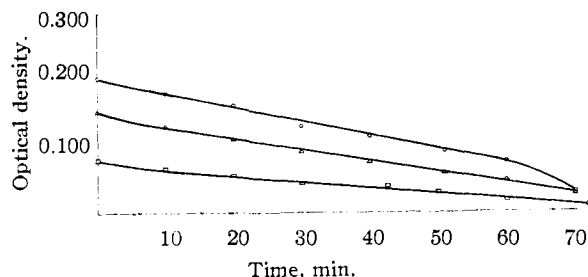
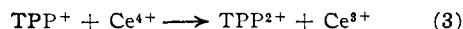
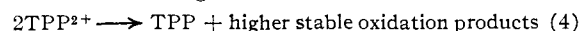


Fig. 3.— $\text{Co}^{60}$  gamma irradiation TPP in 90% propionic acid at  $650\text{ m}\mu$ .

specific absorption spectra, no evidence for their existence was established. Nevertheless, a two electron oxidation of tetraphenylporphine, as suggested for syrupy phosphoric acid medium, cannot be ruled out, *viz.*



The two electron oxidation products of tetraphenylporphine being unstable will rapidly disproportionate according to



In explaining our results of the irradiation of tetraphenylporphine in organic acids, the work of Fricke,<sup>5</sup> Hart,<sup>6</sup> Garrison<sup>7</sup> and others<sup>8,9</sup> may be adduced. It is suggested that irradiation of organic acids containing water yields OH radicals, H atoms and  $\text{H}_2\text{O}_2$  among other products. In addition Bakh and Saraeva<sup>9</sup> have noted the formation of peracids upon X-irradiation of acetic acid. In the presence of dissolved oxygen, hydrogen atoms react with molecular oxygen to form perhydroxyl

(5) H. Fricke and E. J. Hart, *J. Chem. Phys.*, **2**, 824 (1934); H. Fricke, E. J. Hart and H. P. Smith, *ibid.*, **6**, 229 (1938).

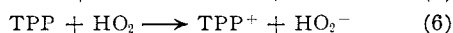
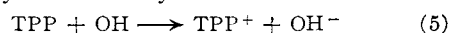
(6) E. J. Hart, (a) *J. Phys. Chem.*, **56**, 594 (1952); (b) *J. Am. Chem. Soc.*, **73**, 68 (1951); (c) *ibid.*, **74**, 4174 (1952); (d) *ibid.*, **76**, 4198 (1954); *ibid.*, **76**, 4312 (1954); (f) *Radiation Research*, **1**, 53 (1954).

(7) (a) W. M. Garrison, D. C. Morrison, H. R. Haymond and J. G. Hamilton, *J. Am. Chem. Soc.*, **74**, 4216 (1952); (b) W. M. Garrison, H. R. Haymond, D. C. Morrison, B. M. Weeks and J. Gile-Melchert, *ibid.*, **75**, 2459 (1953); (c) W. M. Garrison, H. R. Haymond, and B. M. Weeks, *Radiation Research*, **1**, 97 (1954); (d) W. M. Garrison, W. Bennett, S. Cole, H. R. Haymond and B. M. Weeks, *J. Am. Chem. Soc.*, **77**, 2720 (1955); (e) W. M. Garrison, W. Bennett and M. Jayko, *J. Chem. Phys.*, **24**, 631 (1956); (f) W. M. Garrison, H. R. Haymond, W. Bennett and S. Cole, *ibid.*, **25**, 1282 (1956).

(8) W. L. Whitehead, C. Goodman and I. A. Breger, *J. chim. Phys.*, **48**, 184 (1951).

(9) N. A. Bakh and V. V. Saraeva, Symposium on Radiation Chemistry, Academy of Sciences of the USSR, Division of Chemical Science, Editor in Chief: Prof. N. A. Bakh, Moscow, 1955, pp. 145-151.

radicals. Both hydroxyl and perhydroxyl radicals, powerful oxidizing agents, are capable of oxidizing the tetraphenylporphine. Therefore, possible reactions involving oxidation of tetraphenylporphine by radicals may be written as



The corresponding two electron oxidation of tetraphenylporphine with radicals may be written



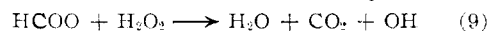
Two electron oxidation of tetraphenylporphine has been suggested with phosphoric acid as a solvent.<sup>1,10</sup>

The increase in the rate of oxidation of tetraphenylporphine with the decrease of the concentration of the acid supports the suggestion that the oxidation of tetraphenylporphine is due to radicals produced upon irradiation of water in the system. The decrease of the concentration of acid is equivalent to the increase of water content. Therefore, more radiation is absorbed by water causing formation of more radicals. On the other hand, there is a competition for the hydroxyl and perhydroxyl radicals between the tetraphenylporphine and organic acid molecules. Thus, at lower acid concentrations radicals have more opportunity to interact with the tetraphenylporphine. Additional evidence for a radical mechanism can be drawn from the fact that there is an increase in the rate of oxidation with an increase in the concentration of tetraphenylporphine.

The initial slope of the curve is a good measure of the stability of the tetraphenylporphine toward ionizing radiation when dissolved in organic acids. It was found that this stability of tetraphenylporphine in organic acids decreases with the increase of the number of carbon atoms of the acid. The result could be predicted on the basis of reactivity of organic acids with oxidizing agents and the scavenging effect of formic acid, acetic acid and propionic acid for the free radicals. After

20 minutes of irradiation of tetraphenylporphine in 90% organic acids, the decrease in the optical density, *i.e.*, the decrease in the concentration of tetraphenylporphine, was 18% for formic acid, 28% for acetic acid and 41.5% for propionic acid.

An explanation of the sharp drop in the optical density of the Soret band and the band in the red region may be offered by taking into account the following considerations. Hart<sup>6a</sup> found that oxygen is converted quantitatively to hydrogen peroxide in aqueous formic acid under the influence of  $\gamma$ -rays. In the presence of excess oxygen, the hydrogen peroxide formed is not decomposed but accumulates. Our experiments have shown that small amounts of hydrogen peroxide do not react with the tetraphenylporphine dissolved in organic acids. Therefore, it may be postulated that the first portion of the curve (in Figs. 1, 2, 3) represents the oxidation of tetraphenylporphine by hydroxyl and perhydroxyl radicals which escaped recombination or interaction with organic acid molecules. It is further postulated that after 22 minutes of irradiation, all oxygen present in the formic acid solution was converted to hydrogen peroxide. In the absence of oxygen, a reaction between hydrogen peroxide and formate radical takes place<sup>6a</sup>



The sharp drop may be considered as a sum of contributions to the oxidation of tetraphenylporphine by hydroxyl radicals, produced by hydrogen peroxide decomposition in oxygen free solution, hydrogen peroxide, which is now present in such concentrations as to be able to interact with tetraphenylporphine, as well as by hydroxyl radicals formed by the primary decomposition of water molecules. Additional support that the sharp drop in optical density is due to the hydrogen peroxide which accumulates to reach a certain concentration to be able to react with tetraphenylporphine can be drawn from the fact that the G value for hydrogen peroxide formation in formic acid is about 2.5 times greater than that in acetic acid.<sup>6a,9</sup> This result is in rough agreement with the time required for rapid decomposition, 22 minutes and 45 minutes respectively observed in the two acids.

(10) P. George and J. M. Goldstein, abstracts of papers read at 129th A. C. S. Meeting, Dallas, Texas, April, 1956, Division of Physical and Inorganic Chemistry, p. 130.