by the procedure of Fischer and Hummel,[2] and of Schumm.[3] The procedure involves three steps: fusion of hemin with resorcinol, demetalation of deuterohemin by a reducing mixture, and esterification of deuteroporphyrin. Recently Walter[4] reported a yield of 26.3% after the method of Fischer, *et al.*[2,5] A yield as high as 46.2% was obtained by us, when we increased the proportion of hemin and resorcinol to 1:5 and used iron powder in acetic acid and hydrochloric acid for demetalation as described by Corwin and Krieble.[6]

A much simpler method was worked out for preparation of the porphyrin directly from red blood cells. Demetalation takes place during the resorcinol fusion and a lengthy procedure of preparing hemin[7,8] from red blood cells is omitted.

In place of resorcinol, two of its derivatives, orcinol and 4-chlororesorcinol, were also tried. The former was found to give a comparable yield with resorcinol, while the latter gave a lower yield.

Paper chromatography[9] has been used as a guide to the purity of the product in these preparations.

Experimental

Preparation from Hemin and Resorcinol.—A sample of 100 mg. of hemin was thoroughly mixed with 500 mg. of resorcinol in an erlenmeyer flask and fused in an oil-bath at 190–200° for 15 minutes. The reaction mixture was then dissolved in 50 ml. of glacial acetic acid and 0.5 ml. of concd. HCl, treated with 50 mg. of iron powder and boiled for 10 minutes. It was then diluted with an equal volume of water, mixed with 80 ml. of saturated solution of sodium acetate and extracted with 50 ml. of ethyl acetate. The extraction was repeated twice with 25-ml. portions of ethyl acetate. The porphyrin in ethyl acetate solution was transferred into 5% HCl and returned to ethyl acetate. After removal of the solvent, the residue was esterified with 20 ml. of CH_3OH–H_2SO_4 (20:1) overnight. The ester was successively extracted with ethyl acetate, 5% HCl, and immediately transferred into chloroform. The chloroform extract was washed with 10 ml. of water four times. Crystals of the porphyrin ester separated out on standing. The yield after recrystallization from chloroform and methanol was 46.2 mg.

Preparation from Red Blood Cells (RBC) and Resorcinol.—A sample of 20 ml. of RBC about 2 months old was treated with 400 ml. of a solution of 1% oxalic acid in acetone according to a procedure[10] previously described. The residue weighing about 2 g. was fused with 5 times its weight of resorcinol as before. The fusion mass without any other treatment was extracted with ethyl acetate. After the porphyrin was transferred back from 5% HCl to ethyl acetate, it was esterified and extracted. The yield of porphyrin ester was 40.4 mg.

The yield and purity of the product depend upon the age of the blood used. When a sample of 7 g. of hemoglobin (Eastman Kodak Co.) was used instead of RBC, the yield of porphyrin ester was 7.2 mg.

When orcinol was used in the place of resorcinol in the fusion mixture, 20 ml. of RBC yielded 39.8 mg. of porphyrin ester. When 4-chlororesorcinol was used, the yield from 20 ml. of RBC was 30.0 mg.

Further Purification of Deuteroporphyrin IX Dimethyl Ester.—As shown in the papergram (Fig. 1), the crystalline porphyrin ester was contaminated with traces of several unknown porphyrin products which will be described in a later publication. Therefore it was chromatographed on a column of $CaCO_3$. Chloroform–benzene mixture (1:3) was used as the developing agent. The deuteroporphyrin ester constituted the lowest compact zone of the chromatogram, which was then cut out, repacked in a sintered glass funnel, and eluted with chloroform. After recrystallization from chloroform and methanol fine and microscopically uniform needles of deuteroporphyrin IX dimethyl ester were obtained, m.p. 223°. The absorptions of the product in ethyl acetate at 621, 568, 527 and 498 mμ, and in 5% HCl at 590 and 547 mμ were read. Its copper complex was also prepared in very fine and shining red needles, m.p. 234°. Its absorptions in ethyl acetate at 558 and 523 mμ, in acetic acid at 559 and 523 mμ were observed. Fischer and Lindner[11] reported a m.p. of 230° for the copper complex.

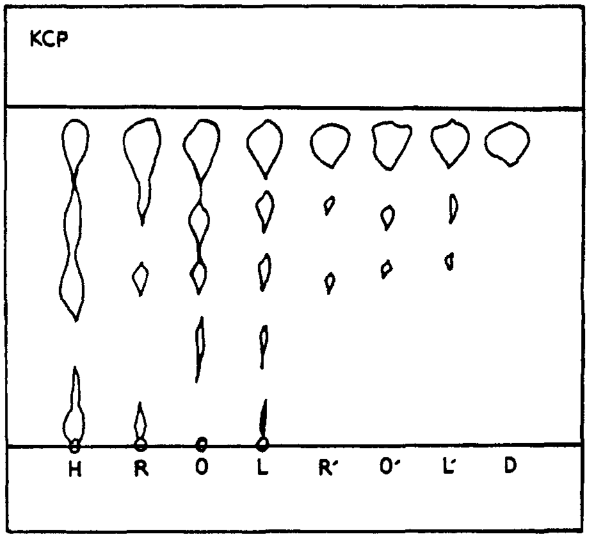

Fig. 1.—Papergrams of crude and purified deuteroporphyrin IX dimethyl ester from different sources. The developing solvent system, KCP, composed of 3.5 ml. of kerosene, 3 ml. of chloroform and 0.2 ml. of 1-propanol under chloroform atmosphere. H stands for the crude porphyrin ester prepared from hemoglobin and resorcinol, R that from RBC and resorcinol (hemin products followed the same pattern as R), O from RBC and orcinol, L from RBC and 4-chlororesorcinol, R′, O′ and L′ the corresponding recrystallized products, and D the chromatographically purified deuteroporphyrin IX dimethyl ester.

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Iodine Inhibition in the Flash Photolysis of Methyl Iodide

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The photolysis of methyl iodide vapor with mercury arc light sources has been studied in some detail.[1-3] The quantum yield is small, due to reac-

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tion of methyl radicals with iodine (iodine inhibition). The decomposition that is observed is due to reaction of energized methyl radicals from the primary photodecomposition with methyl iodide to give methane. These two reactions keep the methyl concentration so low that there is little ethane formation. When iodine was removed by silver foil, the ethane yield greatly increased.[2,3] The possibility of recombination of methyl radicals on the silver or silver iodide surface was not excluded in these experiments.

The availability of a high intensity flash lamp suggested the possibility of generating such a high concentration of methyl radicals that the relative proportions of the products of the reaction might be materially changed. At high intensities, the relative rate of the methyl–methyl reaction should increase, depending as it does on the square of the methyl concentration, so that the importance of methane formation should decrease, and iodine inhibition should set in gradually. This has been observed.

Experimental

A 1-μf condenser charged to 10,000 volts was discharged through a xenon–hydrogen mixture in a quartz tube 15 cm. long and 5 mm. i.d., giving a flash of about 5 μsec. duration, as observed with an oscilloscope.[4] The life of the tube is several thousand flashes. Spectra taken with a small Hilger quartz prism spectrograph show that the lamp gives no significant amount of radiation below 2250 Å., while above this limit there is a many line spectrum with some continuous background. Aluminum reflectors, plain or coated with magnesium oxide, were used behind the lamp and reaction cell. The lamp delivered to the 35-cc. quartz reaction cell (2.1 cm. diam. × 10 cm. long) about 10^{16} quanta per flash in the region of the spectrum absorbed by methyl iodide. This was determined by photolysis in the same apparatus of hydrogen iodide or of methyl iodide in the presence of oxygen.

Eastman Kodak Co. white label methyl iodide was purified by washing with solutions of potassium iodide, sodium hydroxide, sulfuric acid and sodium carbonate, interspersed with washings with water; dried with calcium chloride; and distilled from P_2O_5. A middle fraction of vapor pressure 140 mm. at 0° was stored under vacuum at $-80°$. The best value for the vapor pressure of methyl iodide is probably that of Stull,[5] 141 mm. at 0° (interpolated). This methyl iodide was distilled with refluxing into the reaction cells, after a first portion had been discarded and the vapor pressure checked at 0°.

All experiments were done in the presence of about 600 mm. of Linde argon, which was stated to be free of oxygen, and to contain as principal impurity, less than 0.2% of nitrogen. In some experiments reagent grade iodine was allowed to diffuse into the cell through one stopcock greased with Apiezon N grease.

The photolysis was carried out in a cell in which the gases could be circulated by a thermal siphon through a trap at $-25°$ to prevent accumulation of iodine. This maintained the iodine pressure at 2×10^{-3} mm., corresponding to 2×10^{15} I_2 molecules in the cell, as compared to 3×10^{16} quanta per flash absorbed by methyl iodide. After a number of flashes this cell could be placed directly in a Beckman model DU spectrophotometer and the iodine vaporized from the trap thus determined.

Results.—By comparing the amount of iodine produced in experiments in which it was prevented from accumulating, with the iodine production in the photolysis of methyl iodide in the presence of oxygen, which is stated[6] to have a quantum yield of I_2 of $^1/_2$; the quantum yield of I_2 in the photolysis of methyl iodide at 25° in the presence of 2×10^{-3} mm. of I_2 and 600 mm. of argon was calculated to be 0.2. When iodine is allowed to accumulate during the photolysis, the differential yield at 60° drops to 0.005 after 1000 flashes, at an iodine pressure of 0.54 mm. West and Schlessinger[2] estimated the yield in the presence of accumulated iodine to be 0.002 and Spence and Wild[1] found 0.008, if the quantum yield for the photoöxidation is 1/2.

Although iodine was the only substance determined in most cases, the products of one photolysis in the absence of iodine were analyzed in a mass spectrograph. To gain greater sensitivity in this analysis, the products not condensable at $-80°$ were refluxed at liquid air temperatures and 90% of the argon slowly distilled off. The products, after 150 flashes on a cell containing 26 mm. CH_3I, were: (moles × 10^7), C_2H_6, 9.3; C_2H_4, 0.61; CH_4, 0.4; I_2, 8.3.

By spectrophotometric analysis for iodine between flashes, it was possible to follow the rate of iodine formation as a function of iodine concentration. Typical results are shown in Fig. 1. The amount of iodine produced per flash increases with increasing light intensity, and with increasing pressure of methyl iodide, but the reproducibility of these effects was too poor to define them quantitatively.

Discussion.—The mechanism of the methyl iodide photolysis involves the reactions

$$CH_3I + h\nu \longrightarrow CH_3 + I \tag{1}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6 \tag{2}$$

$$I + I \longrightarrow I_2 \tag{3}$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \tag{4}$$

$$CH_3 + I \longrightarrow CH_3I \tag{5}$$

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I \tag{6}$$

$$CH_2I + I_2 \longrightarrow CH_2I_2 + I \tag{7}$$

The methyl radical produced in (1) by absorption of wave length 2500 Å. near the absorption maximum of methyl iodide has an excess energy of at least 34 kcal./mole. The results of Schultz and Taylor[3] indicate that it is exclusively these hot methyls that react in (6). They find that methane formation is not inhibited by iodine, but is inhibited by inert gas, which reduces the methyls to thermal energies. In all the experiments reported here, the reaction cell contained about 600 mm. of argon, which should have this effect, and also prevent diffusion to the walls. It seems safe to assume that the rate of iodine formation as a function of iodine concentration will give information about the competition between reaction (2) and reactions (4) or (5), and that methane formation may be neglected for this purpose.[7] It follows from the reaction scheme that the amounts of iodine and ethane formed are equivalent. These conclusions are approximately confirmed by the one mass spectrographic analysis. The present work does not decide whether it is reaction (4) or (5) that is respon-

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(7) NOTE ADDED IN PROOF.—Regardless of the importance of hot methyls, the low steric factor for (6) means that the methyl concentration will be effectively determined by (4) or (5) as soon as iodine inhibition is appreciable.

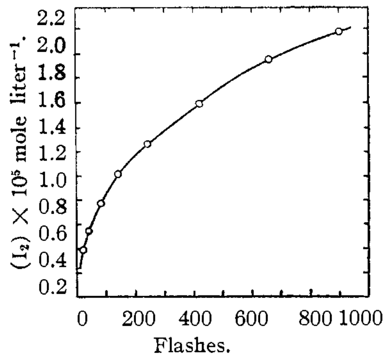

Fig. 1.—Iodine inhibition of iodine formation in the photolysis of methyl iodide. The reaction cell was in an oven at 60°.

sible for iodine inhibition. As I_2 accumulates, the concentration of I atoms formed by photodissociation of I_2 will increase proportionately, and if this is large compared to the concentration of iodine atoms produced by photolysis of methyl iodide, reactions (4) and (5) will both lead to inhibition. The (three body) recombination of iodine atoms is much slower than any of the other important processes.

The methyl radical concentration cannot be calculated by the usual steady state method, and the ratio k_2/k_4 cannot be obtained directly from analysis of final products. The reactions produced by the 5 µsec. flash go to completion in a time which may be comparable to the duration of the flash, as will be seen below. The time variation of the light intensity must be included in the differential rate equation. Observations with an oscilloscope indicate that the light curve may be approximated by an exponential. The rate of formation of methyl radicals is then

$$\mathrm{d}(\mathrm{CH_3})/\mathrm{d}t = S/V \exp(-\beta t) - k_4(\mathrm{CH_3})(\mathrm{I_2}) - k_2(\mathrm{CH_3})^2 \quad (8)$$

written on the assumption that iodine inhibition is due to reaction (4). The first term on the right is the rate of absorption of light per unit volume. In most of the experiments the methyl iodide pressure was low enough so that no large fraction of the light was absorbed near the wall of the cell. As soon as iodine inhibition is appreciable, the third term on the right will be much less important than the second, and may be neglected. The solution of the resulting equation is

$$(\mathrm{CH_3}) = \frac{S}{(\alpha - \beta)V}(\exp(-\beta t) - \exp(-\alpha t)) \quad (9)$$

in which $\alpha = k_4(\mathrm{I_2})$. The total amount of ethane formed during a single flash is then

$$\frac{V}{2}\int_0^\infty k_2(\mathrm{CH_3})^2\mathrm{d}t = \frac{k_2S^2}{4V\alpha\beta(\alpha + \beta)} \quad (10)$$

If the number of flashes is treated as a continuous variable f, this is $V\mathrm{d}(\mathrm{C_2H_6})/\mathrm{d}f$ or $V\mathrm{d}(\mathrm{I_2})/\mathrm{d}f$. Integration for α gives

$$(\alpha^2/3)(\alpha + 1.5\beta) = k_2k_4S^2f/4V^2\beta \quad (11)$$

and logarithmic differentiation of this gives

$$m \equiv \frac{\mathrm{d}\ln\alpha}{\mathrm{d}\ln f} = \frac{1}{3}\left(\frac{\alpha + 1.5\beta}{\alpha + \beta}\right) \underset{\alpha\to\infty}{\longrightarrow} 1/3 \quad \underset{\alpha\to 0}{\longrightarrow} 1/2 \quad (12)$$

From the definition $m(\alpha = 0)/m(\alpha) \equiv 1 + \delta$, one obtains

$$\alpha = 3\delta\beta/(1 - 2\delta) \quad (13)$$

A plot of log $(\mathrm{I_2})$ against log f (Fig. 2) is a straight line of slope $^1/_2$ at $(\mathrm{I_2}) = 10^{-5}$ mole liter^{-1}, and the slope decreases at higher iodine concentrations. By applying equation (13) to Fig. 2, it is estimated that $k_4 = 1.1 \times 10^{10}$ liters mole^{-1} sec.$^{-1}$, where β has been taken as 2.0×10^5 sec.$^{-1}$. Equating the slope of a plot of $(\mathrm{I_2})^2$ against f to the slope given by equation (11) in the limit $\alpha \to 0$, and using $S = 5.5 \times 10^{21}$ quanta per sec. from the photoöxidation experiments, one has $k_2 = 0.6k_4$. The above value of k_4 then gives $k_2 = 7 \times 10^9$ liters mole^{-1} sec.$^{-1}$ at 60° and about 600 mm. of argon. The value of Gomer and Kistiakowsky,[8] obtained with the rotating sector method, is 7.6×10^{10} liter mole^{-1} sec.$^{-1}$ at 60°, corresponding to a steric factor of 1. Durham and Steacie[9] find $k_2 = 1.1 \times 10^9$ liters mole^{-1} sec.$^{-1}$ from a study of the competition of reaction (2) with the reaction of methyl radicals with NO. The result of the present work is only an order of magnitude estimate, but it does give information from a new source on an important reaction of methyl radicals.

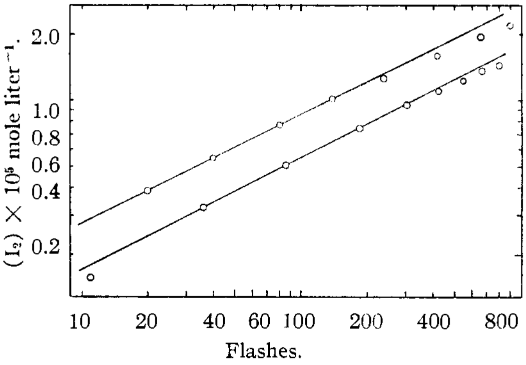

Fig. 2.—Logarithm of iodine concentration as a function of logarithm of number of flashes for two runs. The upper and lower curves have limiting slopes 0.495 and 0.510.

Calculating the collision number using a mean diameter of 4 Å., the value $k_4 = 1.1 \times 10^{10}$ liters mole^{-1} sec.$^{-1}$ corresponds to an activation energy of 0.5 kcal. if the steric factor is unity, or a steric factor of 0.5 if the activation energy is zero. The ratio $k_2/k_4 = 0.6$ is considered to be more reliable than the values of the individual constants. However, it is not certain that our result applies to reaction (4) rather than to (5).

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