Summary

1. It has been found that cyclohexyllithium in large excess reacts with silicon tetrachloride to form chlorotricyclohexylsilane but no tetracyclohexylsilane.

2. Attempts to replace the chlorine atom of chlorotricyclohexylsilane by methyl, ethyl and phenyl groups using both Grignard and organolithium compounds as alkylating agents failed. In addition, this chlorosilane failed to respond to sodium condensation to give the disilane. These results may be due to the steric properties of the three cyclohexyl groups attached to the silicon atom in chlorotricyclohexylsilane.

3. Six new compounds have been prepared and some of their properties described. These compounds are: chlorotricyclohexylsilane, bromotricyclohexylsilane, iodotricyclohexylsilane, acetoxytricyclohexylsilane, tricyclohexylsilane and tricyclohexylsilanol.

MINNEAPOLIS 14, MINN. RECEIVED JUNE 20, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

Photochemical Studies of the Porphyrins. II. The Photoöxidation of Chlorins by Various Quinones

BY FRANK M. HUENNEKENS[1] AND M. CALVIN

Calvin and Dorough[2] have previously established that zinc tetraphenylchlorin is photooxidized in the presence of quinones to zinc tetraphenylporphin. This reaction was studied in great detail for 1,2-naphthoquinone and the following observations made: (1) There is no dark complex formed between the quinone and chlorin. (2) Light adsorbed by the chlorin (6225 Å.) is required. (3) Oxygen inhibits the reaction. (4) The reaction rate is directly independent to the light intensity and inversely related to the temperature. (5) The reaction rate is independent of the naphthoquinone concentration in the range 10^{-3} to 10^{-6} *M*. (The chlorin concentration is initially about 10^{-5} *M*.) (6) A function of the chlorin concentration gives a straight line when plotted against time.

This work has now been extended to include both ortho- and para-quinones (eight in all), as well as measurements on magnesium tetraphenylchlorin.

Experimental

Part 1. Apparatus.—The apparatus and methods were essentially the same as those employed by Calvin and Dorough. The reader is referred to the preceding paper in this series for complete details.[2]

Light Source.—The actinic light was obtained from the tungsten filament lamp (operated at 9 volts) and the monochromator system of a Beckman Quartz Spectrophotometer, Model DU. With the wave length set at 6225 Å. and the slit width at 0.8 mm. the spectral segment was 28.8 Å. In the case of certain para-quinones the reaction was slow; this necessitated focussing the Beckman lamp with great care so that an appreciable reaction could be observed in a matter of a few hours.

Light Intensity Measurements.—After the lamp had been on for at least thirty minutes, the thermostatted cell compartment and phototube housing were removed and a small thermopile (without window) was placed at a fixed, reproducible distance from the front face of the Beckman. At this distance the light beam had an area of 1.77 sq. cm.; the opening of the thermopile was centered in this beam. The intensity of the beam was determined at the beginning and end of each run and the average computed for the mid-point of that run. The thermopile and galvanometer were calibrated with a U. S. Bureau of Standards radiation lamp; the sensitivity was found to be 119.4 watts/sq. cm./cm. deflection. Using the same principles as in the previous paper[2] but with slightly different constants I_0 (in photons/sec.) may be calculated from the galvanometer deflection, D (in cm.), by the following equation: $I_0 = 6.56 \times 10^{14} \times D$.

Reaction Vessel.—The reaction vessel was an ordinary 1-cm. square Pyrex mandrel cell with a magnetic stirrer and an evacuation stopcock built into the cell top (see Fig. 6, reference (2)).

Temperature Control.—Scrupulously clean water, maintained in a large thermostat at 25.0 ± 0.1°, was circulated slowly through the modified Beckman cell compartment with quartz windows. The top of the reaction cell above the water was enclosed in a light-proof cover and heated by a stream of hot air to *ca.* 40°; the heating prevented the benzene solution in the evacuated cell from distilling and condensing on the stirring motor in the upper part of the cell.

Routine Procedure.—In the dark the quinone and chlorin solutions in benzene were mixed: 2.56 cc. of the resultant solution was delivered via a calibrated overflow cup to the reaction cell. The ground glass connection between the top and the bottom of the cell was susceptible to leaks due to striations in the grease caused by the heat and mechanical vibrations of the stirrer. This was remedied by using Cello-Grease No. 14-637, manufactured by the Fisher Scientific Company; the product is guaranteed to maintain its consistency up to 120°. Perfect seals were obtained as follows: The ground glass surfaces at the joint were heated and a thin film of melted grease applied with a brush. The joint was clamped together under light pressure and allowed to cool for thirty minutes. The cell and solution were de-oxygenated by the method of freezing the assembly in liquid nitrogen and evacuating the cell. After thawing the solution, purified hydrogen (passed over hot copper according to the method of Michaelis)[3] was admixed with the vapor phase and the process repeated. Six sweepings with hydrogen were used.

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[1] University of California Fellow in Chemistry, 1947–1948. Present address: The Enzyme Institute, University of Wisconsin, Madison, Wisconsin.

[2] Calvin and Dorough, THIS JOURNAL, **70**, 699 (1948), Paper I of this series.

[3] Michaelis in "Physical Measurements of Organic Chemistry," Vol. II, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1946, p. 1096.

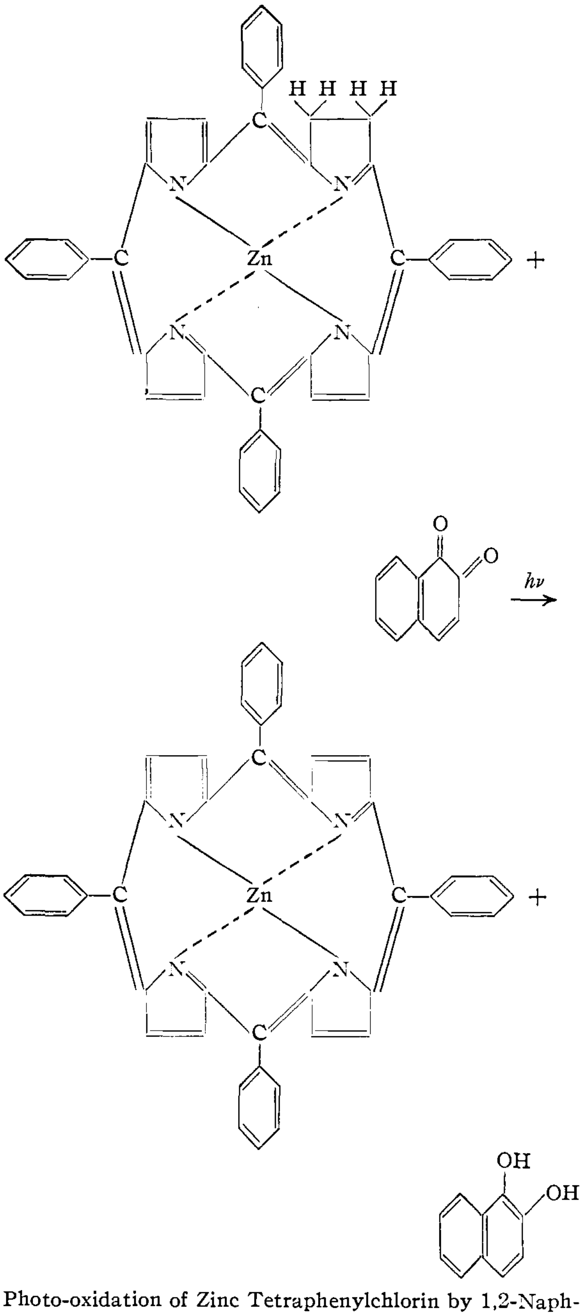

Photo-oxidation of Zinc Tetraphenylchlorin by 1,2-Naphthoquinone

Analytical Method.—After the light intensity had been measured and temperature equilibria established, the cell was illuminated with stirring for several time intervals. At the end of an illumination period the slit width was closed to 0.02 mm., the stirring motor stopped, and the log $1/T$[4] of the solution read for the wave lengths 6225, 5510 and 4650 Å.

Part 2. Materials.—Pure crystalline tetraphenylporphin, tetraphenylchlorin and the corresponding zinc salts were prepared by the methods of Ball, Dorough and Calvin.[5]

Magnesium Tetraphenylchlorin and Porphin.—The reaction was carried out in a standard Grignard apparatus with a bubbler system to remove traces of oxygen in the nitrogen.[6] The reaction flask was charged with 2.5 g. of pure magnesium turnings and the assembly gently heated and swept with nitrogen. Fifteen cc. of an absolute ether solution containing 6.9 cc. of methyl iodide was placed in the separatory funnel and 5 cc. admitted to the flask with gentle stirring. As soon as the reaction began, the remainder of the ethereal solution was added slowly enough to keep the reaction under control. Ten cc. of carefully purified dioxane[7] containing about 1 mg. of tetraphenylporphin was added dropwise through the separatory funnel. The reaction went smoothly, the porphin being converted quantitatively to the magnesium complex and the dioxane causing the magnesium iodide to precipitate. At the conclusion of the reaction 50 cc. of 1 *M* ammonium chloride was added in small portions to decompose the unused Grignard reagent (caution—violent evolution of methane!). The mixture was quantitatively transferred to a separatory funnel, shaken with 35 cc. of benzene and the benzene layer washed three times with 1 *M* ammonium chloride, twice with water and dried over anhydrous sodium sulfate. The benzene solution was concentrated under reduced pressure to about one-third its original volume to remove any residual methyl iodide, ether or dimethylmagnesium and then diluted to 50 cc.

Magnesium tetraphenylchlorin was prepared in the same manner except that all reactions were carried out in near darkness and the product, being photosensitive, had to be stored in a dark-box. Both magnesium porphin and chlorin decompose readily in the presence of acids, or even upon being evaporated to dryness. In addition, the chlorin complex decomposes spontaneously, even in

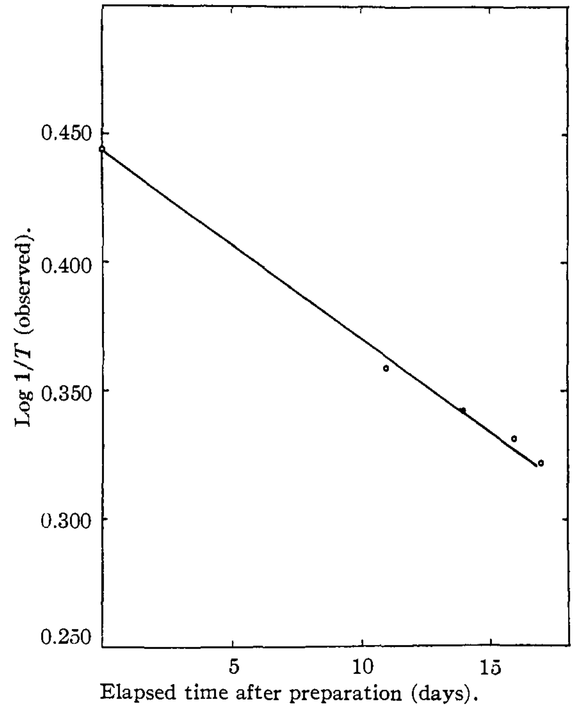

Fig. 1.—Decay of magnesium tetraphenylchlorin as a function of time.

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[4] If T is the fraction of light transmitted and I_0 and I are the incident and outgoing light intensities, respectively, the value of log I_0/I read directly from the Beckman Spectrophotometer is equivalent to log $1/T$.

[5] Ball, Dorough and Calvin, THIS JOURNAL, **68**, 2278 (1946).

[6] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, 1941, pp. 395-404.

[7] *Ibid.*, p. 369.

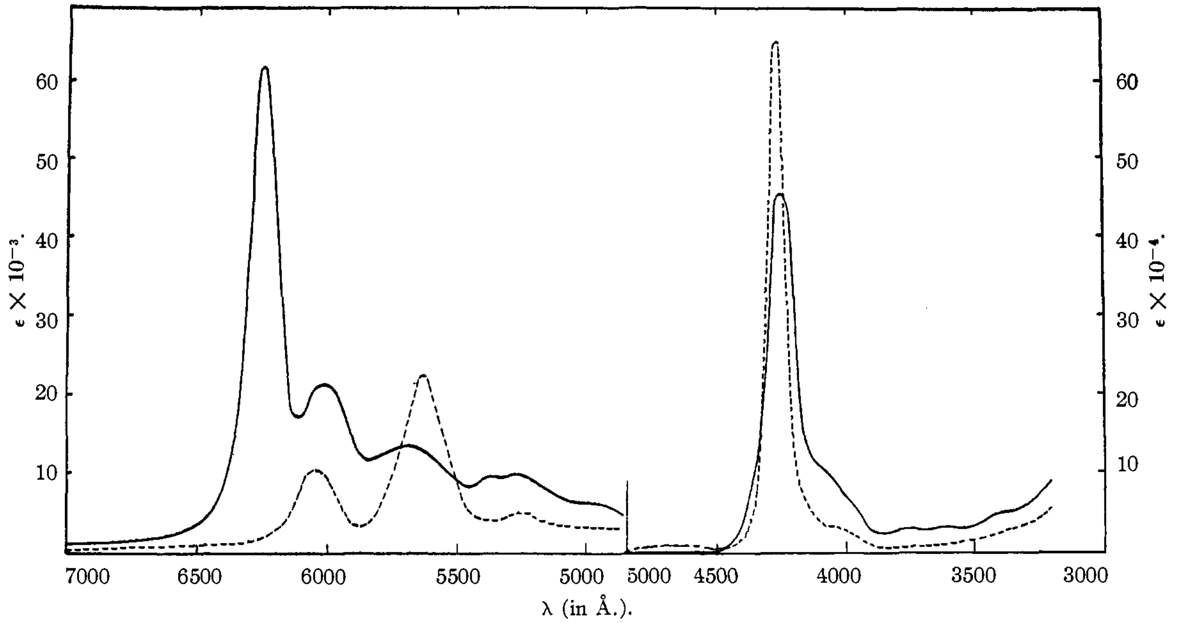

Fig. 2.— - - - Magnesium tetraphenylporphin; — magnesium tetraphenylporphin in benzene.

the dark. The almost linear decrease of concentration with time is shown in Fig. 1. For rate runs the solutions were used within two days after preparation and the initial concentration of magnesium chlorin determined spectrophotometrically.

The concentrations of the magnesium metal complexes were determined by converting an aliquot to the free base. Five cc. of the benzene solution was placed in a separatory funnel and extracted with two 1-cc. portions of concentrated hydrochloric acid. The benzene layer was then washed twice with 5 cc. of water, twice with 5 cc. of concentrated ammonium hydroxide and finally three times with 5 cc. of water. After drying over sodium sulfate, the benzene solution was diluted to 10 cc. The concentration of the free base was determined spectrophotometrically. The absorption spectra of the magnesium complexes are shown in Fig. 2.

Quinones.—9,10-Anthraquinone, 1,2-benz-9,10-anthraquinone, 9,10-phenanthraquinone, 1,4-benzoquinone and 1,4-naphthoquinone were all obtained as stock substances recrystallized from ether or ethyl alcohol.

1,2-Benzoquinone was prepared by oxidizing pyrocatechol with freshly prepared silver oxide in anhydrous ether.[8] The product was a red crystalline powder which decomposed without melting in the range 60–80°. The compound was unstable and decomposed in hydroxylated solvents within a few hours. A solution in anhydrous benzene at 0° stood for several days without decomposition.

1,2-Naphthoquinone (Sample A) was prepared by oxidizing 1-amino-2-naphthol hydrochloride with ferric chloride.[9] The dark golden product was kept as an amorphous cake as recommended by Fieser. At 110–114° the substance darkened and complete decomposition occurred in the region 135–140°.

1,2-Naphthoquinone (Sample B).—The Eastman Kodak product was purified by two sublimations *in vacuo*. The orange needles darkened and decomposed at 110–115°.

Diphenoquinone.—A suspension of 1.0 g. of 4,4'-dihydroxydiphenyl and 20.0 g. of lead dioxide in 50 cc. of anhydrous benzene was boiled gently for five minutes and filtered. The filtrate evaporated to about one-third its original volume, and cooled in an ice-bath yielded crystals of diphenoquinone which were removed by filtration and dried *in vacuo*. Recrystallized once from benzene, the product consisted of orange-red needles with a steely luster and melted at 163–165°.

Part 3. Calculations.—At various times during a rate run log $1/T$ values for three different wave lengths were read from the spectrophotometer. The band at 6225 Å. is characteristic of the zinc chlorin, the band at 5510 Å. is characteristic of the zinc porphin and the band at 4650 Å. is due to the zinc chlorin–oxygen product. The extinction coefficients of these complexes are given in Table I. From the 6225 and 5510 Å. bands the decrease in chlorin concentration (or, conversely, the increase in porphin concentration) may be calculated. A rise in the 4650 Å. band indicates that oxygen is present and competing with the quinone for the chlorin. This effect can be corrected for and the true rate for the quinone–chlorin reaction can be determined. The oxygen–chlorin reaction is treated in another paper.[10]

TABLE I

MOLAL EXTINCTION COEFFICIENTS OF ZINC COMPLEXES

Substance	$\epsilon \times 10^{-3}$		
	6225 Å.	5510 Å.	4650 Å.
Zinc chlorin	54.9	5.9	2.0
Zinc porphin	1.0	22.2	1.8
Zinc chlorin–oxygen product	1.9	7.5	38.7

Any proposed mechanism for the reaction must be consistent with the observations of Calvin and Dorough as set forth in the first section of this paper. Furthermore, anticipating the experimental results, the mechanism must explain why the quantum yield does not vary with quin-

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[8] Willstätter and Pfannenstiel, *Ber.*, **37**, 4745 (1904); Willstätter and Muller, *Ber.*, **44**, 2171 (1911).

[9] Fieser, "Organic Syntheses," **17**, 68 (1937).

[10] Huennekens and Calvin, THIS JOURNAL, **71**, 4031 (1949).

one concentration over a wide range, but, nevertheless, is different for each particular quinone. The key step in the mechanism (No. 6) was suggested to one of the authors (F. H.) by Prof. G. K. Rollefson. The symbols have the following significance: CH_2 = zinc chlorin in the ground state, CH_2^* = zinc chlorin in the excited singlet state, $CH_2^{\mp}$ = zinc chlorin in the triplet state, C = zinc porphin, Q = quinone, QH_2 = hydroquinone, S = solvent and wall.

$$CH_2 + h\nu = CH_2^* \qquad (1)$$

$$CH_2^* = CH_2 + h\nu_f \qquad (2)$$

$$CH_2^* + S = CH_2 + (S + kT) \qquad (3)$$

$$CH = CH_2^{\mp} \qquad (4)$$

$$CH_2^{\mp} + Q = C + QH_2 \qquad (5)$$

$$CH_2^{\pm} + Q = CH_2 + (Q + kT) \qquad (6)$$

Making the usual assumptions about the existence of steady states for both the excited singlet and triplet state molecules, we may write for the disappearance of zinc chlorin

$$\frac{d(CH_2)}{dt} = -\frac{k_5}{k_5 + k_6} \times \frac{k_4}{k_2 + k_3(S) + k_4} \times k_1 I_{abs.} \qquad (7)$$

since the rate of formation of (CH_2^*) is dependent solely on the rate of absorption of light, *i. e.*

$$r_1 = d(CH_2^*)/dt = k_1 I_{abs.} \qquad (8)$$

The conversion factor k_1 must transform photons absorbed per second into moles per liter per second of photons absorbed.

$$k_1 = 10^3/NV \qquad (9)$$

where N is Avogadro's number and V is the volume of the solution (in cc.) The apparent volume delivered to the cell is 2.56 cc.; during pumping some of the solvent is evaporated and the true volume is obtained by employing the equation

$$V = 2.56 \times (C_m/C_0) \qquad (10)$$

where C_m = theoretical concentration of the chlorin solution (allowing for dilution by the quinone solution) and C_0 = the concentration actually determined by the initial reading before illumination.

$I_{abs.}$ may be determined from I_0, the intensity from the Beckman, and an experimental molal extinction coefficient, Σ, of the chlorin

$$I_{abs.} = I_0\,(1 - 10^{-\Sigma(CH_2)d}) = I_0 A \qquad (11)$$

As previously, (CH_2) = the concentration of zinc chlorin and d = the thickness of the cell = 1 cm.

The quantum yield, γ, is expressed by the product of the fractions

$$\gamma = \frac{k_6}{k_5 + k_6} \times \frac{k_4}{k_2 + k_3(S) + k_4} \qquad (12)$$

Substituting equations (8) and (12), equation (7) becomes

$$-\,d(CH_2)/dt = \gamma k_1 I_0 A \qquad (13)$$

Transposing and integrating, letting π represent the integration constant

$$(CH_2) + (1/\Sigma)\log A = -k_1\gamma I_0 t + \pi \qquad (14)$$

The values of (CH_2) are determined from the readings at 6225 Å. Since neither the porphin nor the oxygenated product have any appreciable absorption at this wave length

$$(CH_2) = (\log 1/T)_{obs.}/54.9 \times 10^3 \qquad (15)$$

The values of $(CH_2) + (1/\Sigma)\log A$ are plotted as a function of time and a straight line is obtained. Let M be the slope of the line.

The quantum yield is obtained from the slope of the concentration function–time curve by the equation

$$\gamma = -M/k_1 I_0 \qquad (16)$$

The apparent molal extinction coefficient, Σ, was measured from a chlorin solution with the thermopile–galvanometer under conditions identical with those prevailing during the rate run. The value obtained, $\Sigma = 20.3 \times 10^3$, is smaller than would be expected simply by changing logarithmic bases

$$\Sigma = 54.9 \times 10^3/2.303 = 23.8 \times 10^3$$

The low experimental value is due to the method of measurement. $\epsilon = 54.9 \times 10^3$ was obtained in the usual manner on the spectrophotometer with the slit width set at 0.025 mm. admitting the incident light as a spectral segment of 0.9 Å. When Σ was measured, the slit was opened to 0.8 mm. corresponding to a segment of 28.8 Å. The sharpness of the absorption band and the width of the illuminating band gave rise to the low value of the apparent extinction coefficient.

In the case of magnesium tetraphenylchlorin Σ was 20.5×10^3.

A correction factor of 0.98 was applied to I_0 to compensate for light lost through absorption and scattering by the quartz windows and water of the thermostatted cell compartment.

Part 4. Tabulation of Data.—To avoid unnecessary repetition only one run, no. 54, will be considered in detail. Table II illustrates the data obtained when zinc chlorin was photooxidized by 9,10-phenanthraquinone. The plot of the function $(CH_2) + (1/\Sigma)\log A$ against time is shown in Fig. 3. The results of all runs are summarized in Table III. It is estimated that the quantum yields are accurate to 5–10%, hence the results are expressed only to two significant figures.

TABLE II

RUN NO. 54—ZINC CHLORIN WITH 9,10-PHENANTHRAQUINONE

	log 1/T				
Time	6225 Å.	5510 Å.	4650 Å.	Chlorin concn.	$(CH_2) + (1/\Sigma)$ log A
0	0.508	0.087	0.079	0.926×10^{-5}	-1.30×10^{-5}
15	.471	.093	.075	.857	−1.51
30	.438	.098	.068	.798	−1.70
45	.406	.105	.063	.738	−1.89
96	.314	.123	.052	.572	−2.53

TABLE III

QUANTUM YIELDS OF ZINC TETRAPHENYLCHLORIN

Run	Chlorin concn. × 10^6	Quinone	Quinone concn.	Slope (M) × 10^9	V	$k_1 \times 10^{22}$	D	$I_0 \times 10^{14}$	γ
70	1.25	1,4-Benzo-	2.57×10^{-2}	1.20	2.28	7.23	1.25	8.19	0.0020
71	1.25	1,4-Naphtho-	1.20×10^{-2}	0.819	2.37	6.96	1.13	7.42	.0016
47	1.25	1,4-Naphtho-	3.48×10^{-3}	.567	2.22	7.43	0.84	5.51	.0014
45	1.25	9,10-Anthra-	2.50×10^{-3}	.523	2.14	7.71	0.87	5.71	.0012
59	1.25	9,10-Anthra-	5.00×10^{-5}	.500	2.19	7.53	1.03	6.76	.0010
75	1.25	1,2-Benz-9,10-anthra-	2.33×10^{-3}	1.11	2.39	6.95	1.42	9.32	.0017
76	1.03	Dipheno-	1.30×10^{-4}	1.74	2.40	6.87	1.49	9.77	.0026
46	1.25	9,10-Phenanthra-	2.98×10^{-3}	1.24	2.49	6.62	0.84	5.51	.0034
54	1.25	9,10-Phenanthra-	2.98×10^{-3}	2.08	2.34	7.05	1.10	7.22	.0041
53	1.25	1,2-Naphtho- (A)	4.82×10^{-4}	12.3	2.25	7.33	1.13	7.42	.023
74	1.25	1,2-Naphtho- (B)	7.71×10^{-4}	2.88	2.42	6.82	1.32	8.65	.0049
60	1.09	1,2-Benzo-	1.00×10^{-3}	4.17	2.20	7.50	0.98	6.43	.0086
62	1.25	1,2-Benzo-	3.66×10^{-5}	4.17	2.21	7.47	1.03	6.76	.0083
		Quantum Yields of Magnesium Tetraphenylchlorin							
64	0.658	1,2-Naphtho- (A)	6.50×10^{-4}	Not calculated: —; curved line: $(CH_2) + (1/\Sigma) \log A$ *vs.* time plot					
65	.558	1,2-Naphtho- (A)	7.71×10^{-4}	Not calculated: —; curved line: $(CH_2) + (1/\Sigma) \log A$ *vs.* time plot					
66	.480	1,2-Naphtho- (A)	4.86×10^{-3}	2.07	2.30	7.17	1.50	9.84	.0030
69	.455	1,4-Benzo-	1.27×10^{-2}	0.467	2.20	7.50	1.32	8.66	.00072

Discussion

The energy levels involved in this photochemical transformation may be represented by a Jablonski diagram (Fig. 4). The ground state of the chlorin molecule is a singlet since there are no unpaired electrons; the excited level, due to absorption at 6225 Å., is also a singlet as evidenced by the high transition probability ($\epsilon = 54.9 \times 10^3$). Calvin and Dorough[2] have shown that the chlorin molecules could not be reacting from the S′ state, for not only is the lifetime of this state too short (*ca.* 10^{-9} sec.) compared to the mean time between chlorin–quinone collisions (*ca.* 10^{-5} sec.), but also the chlorin–quinone reaction would compete against fluorescence and solvent deactivation and the quantum yields, therefore, should increase with increasing quinone concentration. Their identification of the triplet as the reactive level was based upon agreement with the kinetic data, direct demonstration of the triplet or phosphorescent state and the greatly reduced quantum yield in the case of the paramagnetic copper chlorin.

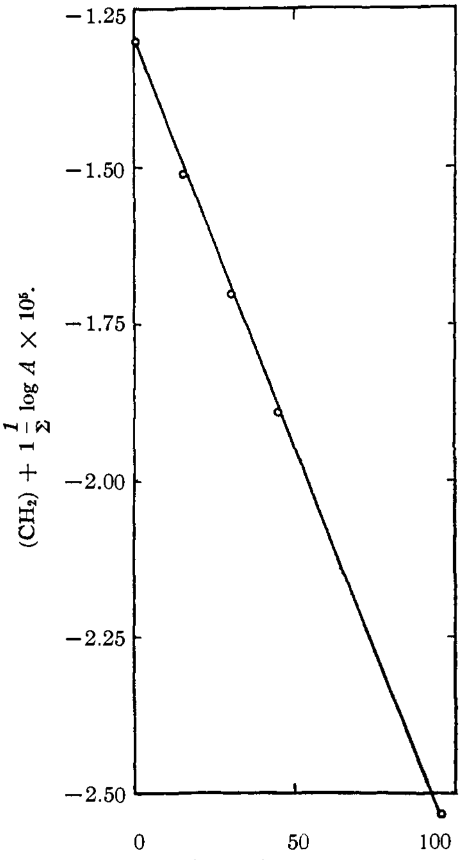

Fig. 3.—Run no. 54.

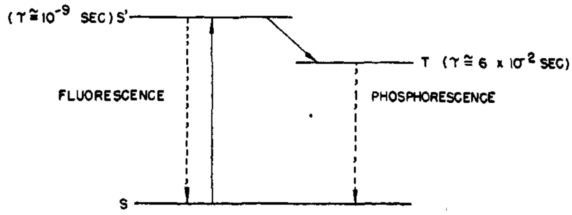

Fig. 4.—Jablonski energy-level diagram.

A very interesting observation, made by these authors, was that the reaction had a negative temperature coefficient. The average quantum yield of four runs at 25° was 0.021 whereas the average of two runs made at 10° was 0.024. In

TABLE IV

QUANTUM YIELDS AND OXIDATION POTENTIALS OF VARIOUS QUINONES

No.	*o*-Quinones	γ	E^{0a}	No.	*p*-Quinones	γ	E_0
1	9,10-Phenanthra-	0.0035	0.41	4	9,10-Anthra-	0.0011	0.25
2	1,2-Naphtho-	.0049	.51	5	1,2-Benz-9,10-anthra-	.0017	.36
3	1,2-Benzo-	.0085	.71	6	1,4-Naphtho-	.0015	.53
				7	1,4-Benzo-	.0021	.71
				8	Dipheno-	.0026	.95

[a] Quinone potentials are taken from G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 311–312. The values are those of E^0 (cor.) rather than E^0 (exp.). The potential is negative when the half-reaction is written: $H_2Q = Q + 2H^+ + 2e^-$.

a later section it will be shown that the absolute value of these quantum yields reported for 1,2-naphthoquinone are subject to an uncertainty. Nevertheless, we shall assume that these relative quantum yields reflect the true behavior of the system and that the magnitude of the temperature effect is beyond normal experimental error.

Kasha and Powell,[11] from an analysis of the rates of the various processes which could occur in the S′ state, have shown that for a maximum probability of interaction between the S′ and T states the "crossing over" must occur at the lowest point of the S′ curve (Fig. 5). Molecules excited to the S′ state may arrive at high vibrational levels but the cascade downward is rapid until a Boltzmann temperature distribution is established among the lower vibrational levels. Since lowering the temperature results in increased quantum yields, it follows that the crossing over point in this case must be located near the bottom of the S′ curve.

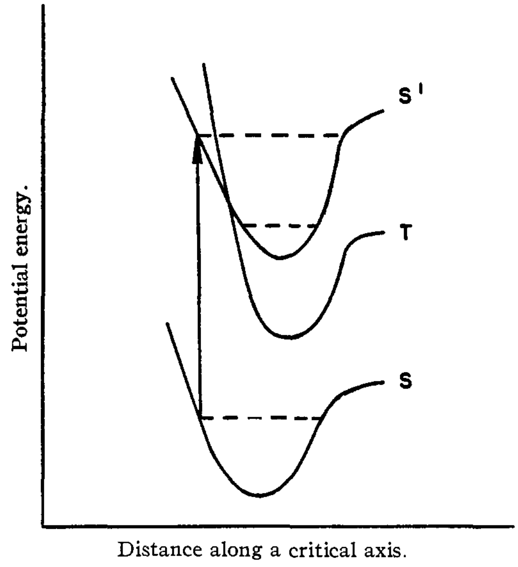

Fig. 5.—Potential energy diagram.

Another effect of lowering the temperature would be to decrease the probability of the back reaction caused by long-lived molecules in the triplet state being thermally reactivated to the S′ state. The separation of the S′ and T minima, estimated from the spectral data, is about 10 kcal.

As illustrated by Table III each quinone has a different quantum efficiency in the photo-oxidation of zinc chlorin. The photo-activation of the chlorin molecules to the triplet level merely loosens the two hydrogen atoms on the β-positions of the pyrrole nucleus. The quinone, which functions as the hydrogen acceptor, removes the hydrogens during collisions with the chlorin. Each quinone–triplet chlorin collision is not effective but the relative efficiency of this process among the various quinones should depend upon the decrease of free energy involved in the reduction of the quinone to the hydroquinone. Thus, the quantum yields should be proportional to some function of the free energy changes. In Table IV a tabulation has been made of the quantum yields and the standard oxidation potentials of the quinones. Plotting these quantities against each other, as in Fig. 6, two straight lines are obtained, one for the ortho-quinones and one for the para-quinones.

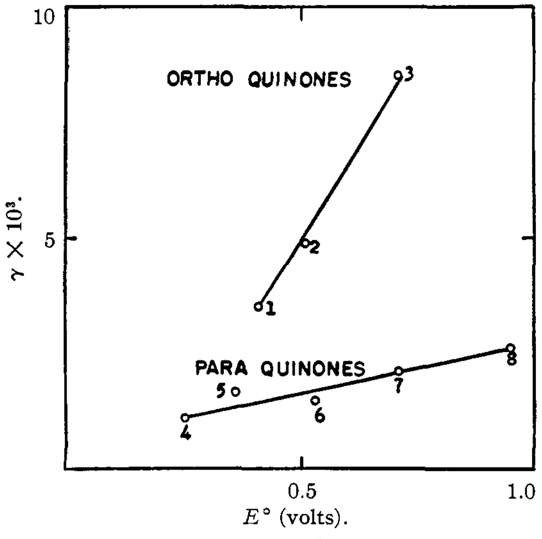

Fig. 6.—Plot of γ *vs.* $E°$ for quinones.

The fact that there are two lines rather than one indicates that the ortho and para-quinones react by different mechanisms. An ortho-quinone may be capable of removing both hydrogens, even in a stepwise manner, during one energetically effective collision, whereas a para-quinone, unable

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(11) Kasha and Powell, This Journal, **69**, 2909 (1947).

to re-orient during the life-time of the activated complex, would require several collisions.

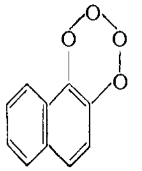
Previous work by Calvin and Dorough[2] on 1,2-naphthoquinone had given a quantum yield of about 0.021. The disagreement between this value and the present results was investigated briefly. The 1,2-naphthoquinone used in the early work had been prepared by the ferric chloride oxidation of 1-amino-2-naphthol hydrochloride. A portion of this material, labeled Sample A, was purified by vacuum sublimation and employed in run no. 53. The quantum yield of 0.023 is in good agreement with the previous value. Next, a sample of Eastman Kodak Co. 1,2-naphthoquinone, labeled Sample B, was purified by vacuum sublimation and, in run no. 74, gave a quantum yield of 0.0049. This value fitted in the *o*-quinone curve of Fig. 6. Samples A and B were compared further on the basis of melting point, analysis and absorption spectra. The results, listed in Table V, indicate only that A had partially decomposed. Sample A was the only quinone, in the series of eight, that was prepared in an aqueous medium. Traces of occluded ferric compounds or quinone peroxides of the types[12] shown

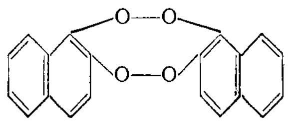
TABLE V

COMPARISON OF PHYSICAL PROPERTIES OF 1,2-NAPHTHOQUINONE

	Sample A	Sample B
Preparation	Ferric chloride oxidation of 1-amino-2-naphthol. Crystallization from water solution	Eastman Kodak Co. stock purified by two sublimations *in vacuo*
Melting point	Darkens at 110–114°, decomposes (to a black oil) 135–140°	Darkens and decomposes 113–114°
Analysis[a]	Calcd. for $C_{10}H_6O_2$ (m. w. 158.2): C, 75.8; H, 3.79%. Found: C, 71.38; H, 4.02; residue, 10.1	Found: C, 76.17, H, 4.29
Absorption spectrum (in benzene)	In the visible region (7000–3500 Å.) both samples displayed the same spectrum. The extinction coefficients were slightly higher for Sample B	

[a] Analysis performed by Mr. C. Koch.





could possibly account for the "enhanced" quantum yields obtained with Sample A.

Less extensive experiments were carried out with magnesium tetraphenylchlorin because of its unstability and the low quantum yields which were difficult to measure.

Runs no. 64 and 65 made with 1,2-naphthoquinone (Sample A) and magnesium chlorin exhibited a curved line plot of $(CH_2) + (1/\Sigma)$ log A against time. At these quinone concentrations (*ca.* 5 × 10^{-4} *M*) an insufficient number of collisions occurred during the triplet lifetime of the magnesium chlorin causing the rate to deviate from the expected straight-line plot. When the concentration was increased to *ca.* 5 × 10^{-3} *M* as in run no. 56, the rate curve was once again a straight line. In the case of zinc chlorin this concentration "breakdown" did not occur until the quinone concentration had been reduced to about 10^{-6} *M*. Hence, either the lifetime of the magnesium chlorin in the triplet state is shorter than the 10^{-2} sec. observed for zinc chlorin or the quantum efficiency of phosphorescence is less for the magnesium complex, *i. e.*, fewer of the molecules reach the triplet state.

A comparison of magnesium and zinc chlorins may be seen in Table VI. The discrepancy of the ratio for 1,4-benzoquinone could be explained simply as a difference between the two classes of quinones or the quantum yield for the reaction with the magnesium chlorin could be in error since the rate was so slow and irregular, in that one run, that the assignment of a slope to the individual points was only an approximation.

TABLE VI

COMPARISON OF ZINC AND MAGNESIUM CHLORINS

Oxidant	γ_{Zn}	γ_{Mg}	Ratio γ_{Zn}/γ_{Mg}
1,4-Benzoquinone	0.0021	0.00072	2.9
1,2-Naphthoquinone (Sample A)	.023	.0030	7.7
Oxygen[10]	.0074	.00094	7.9

An attempt was made to determine the lifetime of the phosphorescent state for magnesium chlorin using a rotating shutter phosphoroscope in conjunction with a photomultiplier tube and an oscilloscope. No decay curve could be observed corroborating the above conclusions regarding the phosphorescence life-time or phosphorescence efficiency of the magnesium chlorin. However, the magnesium chlorin does have a phosphorescent state, for when a sample was placed in a rotating shutter phosphoroscope and exposed to an ammonia-sensitized plate for three hours, a phosphorescence spectrum was obtained qualitatively similar to that of zinc chlorin.[13]

Acknowledgment.—The authors appreciate the many helpful suggestions made by their colleagues, notably Professors G. K. Rollefson and J. Cason and Drs. G. D. Dorough, M. Kasha, D. McClure, W. Simpson and H. W. Alter.

Summary

1. The zinc and magnesium complexes of tetraphenylchlorin may be photoöxidized to the corresponding porphins by both *o*- and *p*-quinones.

2. Plotting the standard oxidation potential of the quinone against the quantum yield produces one straight line for the *o*-quinones and

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(12) Goldschmidt and Graef, *Ber.*, **61**, 1858 (1928).

(13) These measurements were made in the laboratory of Drs. M. Kasha and D. McClure.

another straight line for the *p*-quinones.

3. The rates of photoöxidation for magnesium tetraphenylchlorin are lower than the corresponding zinc chlorin reactions by a factor of almost eight.

RECEIVED APRIL 12, 1949

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

Photochemical Studies of the Porphyrins. III. The Photoöxidation of Chlorins by Oxygen

BY FRANK M. HUENNEKENS[1] AND M. CALVIN

In the previous paper of this series[1a] it was established that the zinc and magnesium complexes of tetraphenylchlorin may be photooxidized to the corresponding porphin utilizing various ortho- and para-quinones as the hydrogen acceptors. Traces of oxygen were found to interfere with the normal quinone–chlorin reaction and a method of de-oxygenating the solution with purified hydrogen was devised. From a biological point of view, molecular oxygen is of great importance for although it possesses a high oxidation potential and is the final electron acceptor in aerobic systems it is, nevertheless, unable to directly oxidize certain compounds; *e. g.*, reduced pyridinoproteins or cytochrome c. It was of interest to ascertain whether in this case oxygen might be competing with the quinone as an oxidant for the photoactivated zinc chlorin.

Experimental

Part 1. Apparatus and Materials.—The apparatus and materials used in these experiments were the same as described in the previous two papers of this series.[1,2]

The ultimate reaction product, called the zinc chlorin–oxygen complex, obtained when oxygen reacts with photo-activated zinc chlorin, was not isolated in pure form. For absorption spectra purposes a known solution of zinc chlorin, in a sealed Pyrex 1-cm. square cuvette, was exposed to bright sunlight for five minutes. The absorption spectrum of this "unbleached," straw-yellow solution was determined as rapidly as possible (within five minutes) using a Cary Recording Spectrophotometer. The molal extinction coefficients were calculated on the basis that conversion of the initial chlorin was quantitative. The "bleached" product was quite stable since the absorption spectrum of a solution, exposed to diffuse laboratory light for several days, did not change appreciably; furthermore, several different zinc chlorin solutions exposed to light under a variety of conditions yielded the identical product.

The absorption spectrum of the metal-free chlorin–oxygen product was obtained by removing the zinc from a known solution of the "bleached" complex by means of the hydrochloric acid–ammonium hydroxide treatment described in a previous paper.[1]

Rate runs in the presence of both oxygen and a quinone were made inadvertently during the early part of this investigation when imperfectly sealed reaction cells permitted small quantities of oxygen to enter. Since the reaction rate is independent of the concentration of the oxidant provided it exceeds a certain minimum (*ca.* 10^{-6} *M* for zinc chlorin), it is, therefore, unnecessary to know the exact amount of oxygen present.

When oxygen alone was the oxidant, 2 cc. of the chlorin solution and 1 cc. of benzene were delivered directly to the reaction vessel and since the solution was not de-oxygenated by freezing, evacuating and sweeping with hydrogen, no volume correction was required.

Part 2. Calculations.—As will be discussed more thoroughly in a later section, oxygen differs from the quinones in that after the primary oxidation of the chlorin to the porphin a secondary reaction takes place in which the hydrogen peroxide reacts further with the porphin to produce a "bleached" yellow product. This does not interfere with the normal measurement of the quantum yield, since of all the substances in solution only the chlorin absorbs the irradiating light (6225 Å.) and the method of following the reaction depends only upon the disappearance of the chlorin.

In the case of 1,4-benzoquinone and 9,10-phenanthraquinone several runs were made in the presence of oxygen. For these runs, the observed quantum yields (γ) has been multiplied by a correction factor (f) to give the hypothetical quantum yield (γ') which would have been obtained if the quinone alone had reacted with the porphin. This correction factor is derived as follows: consider an entire rate run and let

n = total number of chlorin molecules that have reacted (with quinone and oxygen)
n' = number of chlorin molecules that have reacted with oxygen alone
Q = total number of quanta absorbed
γ = measured quantum yield
γ' = quantum yield of the quinone–chlorin reaction only
$A_0 - A$ = change in the log $1/T$ (the usual log I_0/I from the Beckman Spectrophotometer) reading at 6225 Å. for the entire run

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[1] University of California Fellow in Chemistry, 1947–1948. Present address: The Enzyme Institute, University of Wisconsin, Madison, Wisconsin.

[1a] Huennekens and Calvin, THIS JOURNAL, **71**, 4024 (1949).

[2] Calvin and Dorough, *ibid.*, **70**, 699 (1948).